

U.S. DEPARTMENT OF COMMERCE
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PB-255 983

Demetallization of Heavy Residual Oils Phase III

Hydrocarbon Research, Inc.

Prepared For
Industrial Environmental Research Lab.

June 1976

TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)		
1. REPORT NO. EPA-600/2-76-165	2.	3. REPORT'S ACCESSION NO. PD255983
4. TITLE AND SUBTITLE Demetallization of Heavy Residual Oils--Phase III	5. REPORT DATE June 1976	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) M. C. Chervenak, P. Maruhnic, and G. Nongbri	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Hydrocarbon Research, Inc. New York and Puritan Avenues Trenton, New Jersey 08607	10. PROGRAM ELEMENT NO. LAB013; ROAP 21ADD-050	
	11. CONTRACT/GRANT NO. 68-02-0293	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Phase III Final: 1/75-3/76	
	14. SPONSORING AGENCY CODE EPA-ORD	
15. SUPPLEMENTARY NOTES EPA-650/2-73-041 and -041a are earlier reports in this series. IERL-RTP project officer for this report is W. J. Rhodes, Mail Drop 61, 919/549-8411, Ext 2851.		
16. ABSTRACT The report gives results of Phase III work to optimize operating conditions in the demetallization step for overall desulfurization of heavy petroleum residual oils. Bachaquero and Lloydminster vacuum residua were demetallized to different levels of vanadium removal, the products desulfurized over commercial hydrodesulfurization catalyst at various operating conditions, and minimum operating costs were calculated to produce low sulfur fuel oil. The report describes test units, operating conditions, and procedures, and includes run summaries and tables of feedstock, product, and catalyst inspections. Graphs and tables depicting operating costs for producing 0.3, 0.5, and 1.0 wt % sulfur fuel oil are given, along with various correlations between demetallization levels, catalyst deactivation, demetallization rate constant, and contaminant metals deposited on catalyst.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Catalysis Petroleum Industry Operating Costs Residual Oils Fuel Oil Desulfurization Vanadium	Air Pollution Control Stationary Sources Demetallization Hydrodesulfurization	13B 05C 14A, 05A 21D 07A, 07D 07B
18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified	21. NO. OF PAGES 112 22. PRICE 5.50-2.25

229187

PB 255 983

EPA-600/2-76-165

June 1976

Environmental Protection Technology Series



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NATIONAL TECHNICAL
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U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

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EPA-600/2-76-165

June 1976

DEMETALLIZATION
OF HEAVY RESIDUAL OILS
PHASE III

by

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Contract No. 68-02-0293
ROAP No. 21ADD-050
Program Element No. 1AB013

EPA Project Officer: William J. Rhodes

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

ABSTRACT

Under Phase I work of Contract No. 68-02-0293 funded by the Environmental Protection Agency, a new low cost demetallization catalyst for heavy petroleum residual oils was developed at the Trenton laboratory of Hydrocarbon Research, Inc., a subsidiary of Dynallectron Corp. Work under Phase II optimized promoter metal on the support, commercial production capabilities were demonstrated by the production of a 10,000 pound batch by Minerals and Chemicals Division of Engelhard Corporation, and activity and aging characteristics were tested on two vacuum residua. The demetallized products from these two residua were desulfurized over commercial HDS beads and costs were calculated to produce low sulfur fuel oil and compared against costs using unpromoted activated bauxite.

The present Phase III work optimized operating conditions in the demetallization step for overall desulfurization. Rachaquero Export and Lloydminster vacuum residua were demetallized to different levels of vanadium removal, the products desulfurized over commercial HDS catalyst at various operating conditions and minimum operating costs were calculated to produce low sulfur fuel oil.

Descriptions of test units, operating conditions and procedures are given, including run summaries, and tables of feedstock, product and catalyst inspections. Graphs and tables depicting operating costs for producing 0.3, 0.5 and 1.0 weight percent (W %) sulfur fuel oil are given, along with various correlations among demetallization levels, catalyst deactivation, demetallization rate constant and contaminant metals deposited on catalyst.

Conclusions based on experimental results are given.

CONTENTS

	<u>Page No.</u>
Abstract	iii
List of Figures	vii
List of Tables	xi
Glossary	xv
1. CONCLUSIONS	1
2. INTRODUCTION	3
3. EXPERIMENTAL; DEMETALLIZATION	5
3.1 Apparatus and Procedures	5
3.2 Catalyst Description and Inspections	8
3.3 Bachaquero Export Vacuum Residuum; Preparation and Inspections	8
3.3.1 Low Level Demetallization	11
3.3.2 Medium Level Demetallization	15
3.3.3 High Level Demetallization	17
3.4 Lloydminster Vacuum Residuum; Preparation and Inspections	21
3.4.1 Demetallization to 45-60% Vanadium Removal	21
3.4.2 Demetallization to 80-85% Vanadium Removal	25
3.5 Kinetics of Demetallization	25
3.6 Spent Demetallization Catalyst Inspections	28
3.7 Catalyst Deactivation Correlations	31

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CONTENTS

	<u>Page No.</u>
4. EXPERIMENTAL; DESULFURIZATION	35
4.1 Apparatus and Procedures	35
4.2 Catalyst Description and Inspections	35
4.3 Demetallized Bachaquero Export Vacuum Residuum	36
4.3.1 Products from Low Level Demetallization	36
4.3.2 Products from Medium Level Demetallization	36
4.3.3 Products from High Level Demetallization	40
4.4 Demetallized Lloydminster Vacuum Residuum	45
4.4.1 Products from Medium Level Demetallization	45
4.4.2 Products from High Level Demetallization	45
4.5 Spent Desulfurization Catalyst Inspections	49
4.6 Desulfurization Correlations	52
4.7 Correlated Fuel Oil Properties	56
5. PROCESS ECONOMICS	61
6. APPENDICES:	71
A Summary of Demetallization Runs	73
A-1 Demetallization Operating Conditions, Yields and Product Properties	79
B Summary of Desulfurization Runs	89
B-1 Desulfurization Operating Conditions, Yields and Product Properties	97

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
1	Fixed Bed Demetallization Unit	6
2	Fixed Bed Demetallization Reactor	7
3	Demetallization Catalyst HRI 3634	10
4	Demetallization of Bachaquero Export Vacuum Residuum Over 1.0 W % Molybdenum/ 20x50 Mesh Bauxite	13
5	Desulfurization Obtained During Demetal- lization of Bachaquero Export Vacuum Residuum Over 1.0 W % Molybdenum/20x50 Mesh Bauxite	14
6	Demetallization and Desulfurization Obtained During Demetallization of Bachaquero Export Vacuum Residuum Over 1.0 W % Molybdenum/20x50 Mesh Bauxite	16
7	Demetallization of Bachaquero Export Vacuum Residuum Over 1.0 W % Molybdenum/ 20x50 Mesh Bauxite	19
8	Sulfur and Nickel Removals as Function of Vanadium Removal During Demetallization of Bachaquero Export Vacuum Residuum on 1 % Molybdenum/20x50 Mesh Bauxite	20
9	Demetallization of Lloydminster Vacuum Residuum Over 1 W % Molybdenum/20x50 Mesh Bauxite	23
10	Desulfurization Obtained During Demetal- lization of Lloydminster Vacuum Residuum Over 1 W % Molybdenum/20x50 Mesh Bauxite	24
11	Sulfur and Nickel Removal as Function of Vanadium Removal During Demetallization of Lloydminster Vacuum Residuum on 1 % Molyb- denum/20x50 Mesh Bauxite	26

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
12	Kinetics of Demetallization	27
13	Effect of Level of Vanadium Removal on the Rate of Catalyst Deactivation	32
14	Variation of Demetallization Rate Constant with Vanadium Loading on the Catalyst	33
15	Desulfurization of Low Level (40-45% Vanadium Removal) Demetallized Bachaquero Export Vacuum Residuum Over 0.02" HDS Beads	39
16	Desulfurization of Medium Level (65-70% Vanadium Removal) Demetallized Bachaquero Export Vacuum Residuum Over 0.02" Beads	41
17	Desulfurization of Medium Level (65-70% Vanadium Removal) Demetallized Bachaquero Export Vacuum Residuum Over 0.02" Beads	42
18	Desulfurization of High Level (80-85% Vanadium Removal) Demetallized Bachaquero Export Vacuum Residuum Over 0.02" Beads	43
19	Desulfurization of Demetallized Bachaquero Export Vacuum Residuum. Liquid Product Sulfur	44
20	Desulfurization of Demetallized Lloydminster Vacuum Residuum Over 0.02" Beads	47
21	Desulfurization of Demetallized Lloydminster Vacuum Residuum Over 0.02" Beads. Liquid Product Sulfur	48
22	Effect of Metals Content of Demetallized Feeds on Deactivation Slope of the Desulfurization Catalyst	53

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
23	Metals Level in Demetallized Feed Versus Metals Loading of Desulfurization Catalysts	54
24	Effect of Level of Desulfurization On De- activation Slope of Desulfurization Catalysts	55
25	Fuel Oil Viscosity Vs. °API	57
26	400°F+ Fuel Oil Viscosity Vs. Pour Point	58
27	650°F+ Fuel Oil Viscosity Vs. Pour Point	59
28	Total Operating Cost for a Two Stage Demetallization-Desulfurization of Bachaquero Export Vacuum Residuum	64
29	Total Operating Cost for a Two Stage Demetallization-Desulfurization of Lloydminster Vacuum Residuum	66
30	Total Operating Cost for a Two Stage Demetallization-Desulfurization Versus Direct Desulfurization	67

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
1	Demetallization Catalyst Inspections	9
2	Feedstock Inspections-Bachaquero Export V. R.	12
3	Feedstock Inspections-Lloydminster V. R.	22
4	Analyses of Spent Demetallization Catalysts	29
5	Pore Size Distribution of Spent Demetallization Catalysts	30
6	Summary of Inspections on American Cyanamid 0.02" High Activity Beaded Catalyst	37
7	Feedstock Inspections-Demetallized Bachaquero Export V. R.	38
8	Feedstock Inspections-Demetallized Lloydminster V. R.	46
9	Analyses of Spent Desulfurization Catalysts	50
10	Pore Size Distribution of Spent Desulfurization Catalysts	51
11	Investment and Operating Cost for a Two-Stage Demetallization-Desulfurization Operation of Bachaquero Export Vacuum Residuum	62
12	Investment and Operating Cost for a Two-Stage Demetallization-Desulfurization Operation of Lloydminster Vacuum Residuum	63
13	Estimated Overall Yields and Product Properties from Consecutive Demetallization and Desulfurization of Bachaquero Export Vacuum Residuum	69
14	Estimated Overall Yields and Product Properties from Consecutive Demetallization and Desulfurization of Lloydminster Vacuum Residuum	70

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LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
A	Summary of Demetallization Runs	73
A-1	Operating Conditions, Yields, and Product Properties-Run 115-1233-5B	79
A-2	Operating Conditions, Yields, and Product Properties-Run 115-1238-4	82
A-3	Operating Conditions, Yields, and Product Properties-Run 115-1238-14	83
A-4	Operating Conditions, Yields, and Product Properties-Run 115-1240-3	84
A-5	Operating Conditions, Yields, and Product Properties-Run 115-1240-8	85
A-6	Operating Conditions, Yields, and Product Properties-Run 115-1248-9B	86
A-7	Operating Conditions, Yields, and Product Properties-Run 115-1249-9	87
B	Summary of Desulfurization Runs	89
B-1	Operating Conditions, Yields, and Product Properties-Run 184-194-17	99
B-2	Operating Conditions, Yields, and Product Properties-Run 184-195-4	100
B-3	Operating Conditions, Yields, and Product Properties-Run 184-195-19	101
B-4	Operating Conditions, Yields, and Product Properties-Run 184-196-4	102
B-5	Operating Conditions, Yields, and Product Properties-Run 184-196-20	103
B-6	Operating Conditions, Yields, and Product Properties-Run 185-248-3	104

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
B-7	Operating Conditions, Yields, and Product Properties-Run 185-248-11	105
B-8	Operating Conditions, Yields, and Product Properties-Run 185-249-4	106
B-9	Operating Conditions, Yields, and Product Properties-Run 185-249-15	107
B-10	Operating Conditions, Yields, and Product Properties-Run 185-250-14	108
B-11	Operating Conditions, Yields, and Product Properties-Run 185-250-25	109
B-12	Operating Conditions, Yields, and Product Properties-Run 185-251-4	110
B-13	Operating Conditions, Yields, and Product Properties-Run 185-251-20	111

GLOSSARY

MM	Millions
1 Angstrom ($\text{\AA}$)	10^{-8} Centimeters
g/cc	Grams/cubic centimeter
M^2/g	Square meters/gram
Mesh Sizes	Mesh sizes are all United States Standard Sieve Series
psig	Pounds per square inch, gauge
SCF/Bbl	Standard cubic feet of gas per barrel of oil (60°F, 1 Atm.)
L.S.V.	Liquid Space Velocity, Volume of Oil/Hour/ Volume of Reactor
Vo/Hr/Vr	Volumes of Oil/Hour/Volume of Reactor
MMB	Million Barrels
Bbl/D/Lb	Barrels of Oil/Day/Pound of Catalyst
BPSD	Barrels per Stream Day
ppm	Parts per million
SFS	Saybolt Furoi Seconds
SUS	Saybolt Universal Seconds
VB	Vacuum Bottoms = Vacuum Residuum

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1. CONCLUSIONS

The newly developed demetallization catalyst, granular 20 x 50 mesh activated bauxite impregnated with 1.0 weight percent molybdenum, when used in the first stage of a two-stage demetallization desulfurization process, offers a substantial operating cost advantage over a direct desulfurization process in the production of low sulfur fuel oil from high metals petroleum vacuum residua.

For a typical case on Bachaquero Export vacuum residuum, a high metals stock from Venezuela, the saving in operating cost to produce 0.3 weight percent fuel oil was \$1.15/Bbl, to produce 0.5 weight percent sulfur fuel oil the saving was \$0.78/Bbl, and a saving of \$0.44/Bbl was realized to produce 1.0 weight percent sulfur fuel oil. Similar cost advantages were realized in the production of low sulfur fuel oils from Lloydminster vacuum residuum, a high sulfur Canadian stock.

These cost calculations were based on a 20,000 barrels per day plant, which is perhaps the minimum size plant a refiner would build. Operating costs would be lowered as the size of the plant is increased resulting in increased savings.

The optimum demetallization level to achieve minimum overall operating costs from Bachaquero Export to produce 1.0 weight percent sulfur fuel oil was about 45 percent vanadium removal. To produce 0.5 weight percent sulfur fuel oil to optimum demetallization level was about 55 percent vanadium removal. For the production of 0.3 weight percent sulfur fuel oil the operating costs decreased with increasing levels of vanadium removal. However, levels above 80 percent vanadium removal were difficult to achieve because of the rapid rate of catalyst deactivation, but removal of metals above this level are believed to be of dubious economic value, since these metal compounds are difficult to remove by the demetallization catalyst, they would also be difficult to remove by the commercial desulfurization catalyst.

For Lloydminster vacuum residuum, the optimum demetallization level to produce 1.0 weight percent sulfur fuel oil was about 65 percent vanadium removal. To produce 0.5 weight percent sulfur fuel oil the level was 75 percent and for 0.3 weight percent sulfur fuel oil the optimum level was about 85 percent vanadium removal.

2. INTRODUCTION

Because of more stringent federal environmental pollution standards along with the increased demands for energy in the 1970's, the need for and value of clean low sulfur fuel oil has been well established and documented. Given the finite nature of fossil fuels, full and best use of all petroleum fractions is not only desirable but imperative if we are to meet the energy demand before alternative sources are developed.

There are substantial reserves of high sulfur petroleum resids, foreign and domestic, containing contaminant metals vanadium and nickel, which rapidly poison HDS catalysts and render the overall processing of these resids economically unattractive. In order to improve removal of contaminants from these fuels while economically producing low sulfur fuel oil from petroleum resids, HRI undertook a project funded by the Environmental Protection Agency, under Contract No. 68-02-0293, to develop a low cost scavenger catalyst to remove contaminant metals from petroleum resids prior to desulfurization over commercial HDS catalysts.

In Phase I work of the present contract, a literature review was made for guidance in choosing catalyst supports and promoter metals for possible development. After evaluating catalyst supports, alumina, silica-alumina, bauxites, clays and solid carbons, activated bauxite was found to be the best support of those tested in terms of availability, low cost and relatively high demetallization activity. To further improve activity, activated bauxite was impregnated with promoter metals, V, Cr, Mo, W, Fe, Co, Ni, B, Mn, and Zn. It was found that low levels of molybdenum on activated bauxite was most effective in terms of demetallization activity, aging characteristics and surprisingly high desulfurization activity considering the low molybdenum loading.

Under Phase II work, optimization of molybdenum loading on activated bauxite was found to be 1.0 weight percent and particle size for fixed bed operations to be 20 x 50 mesh. To demonstrate commercial production capability, Minerals and Chemicals Division of Engelhard Corporation produced a 10,000 pound batch on commercial production equipment. The newly developed commercially produced catalyst was tested for activity and aging characteristics followed by desulfurization of the demetallized products over a commercial HDS catalyst. Preliminary costs to produce low sulfur fuel oil from Tia Juana and Gach Saran vacuum residua were calculated and found to offer substantial cost advantages.

over unpromoted bauxite in the demetallization step of a two stage system.

The objectives under the present Phase III work were to optimize operating conditions in the demetallization and desulfurization steps in order to obtain more accurate cost figures to produce low sulfur fuel oil. The oils used for this phase were Bachaquero Export and Lloydminster vacuum residua. Bachaquero Export vacuum residuum, a high metals Venezuelan stock, was demetallized to three levels of vanadium removal (45, 65 and 83%), the blended products desulfurized over commercial HDS beads, and operating costs were calculated to produce 1.0, 0.5, and 0.3 weight percent sulfur fuel oils. Lloydminster vacuum residuum, a high sulfur medium metals stock from Canada, was demetallized to two levels of vanadium removal (63 and 85%), desulfurized over commercial HDS beads and costs calculated to produce low sulfur fuel oil.

The operating costs and plant investment for producing low sulfur fuel oil from Bachaquero Export and Lloydminster vacuum residua were compared to costs using a direct desulfurization process.

3. EXPERIMENTAL; DEMETALLIZATION

3.1 Apparatus and Procedures

All demetallization operations were carried out in a continuous downflow, fixed bed reactor system. Figure 1 shows a schematic diagram of Unit 115 having two reactors connected in series contained in a single lead bath. Each reactor shown in Figure 2 was fabricated from $1\frac{1}{2}$ " O.D. by 1" I.D. stainless steel tubing, and has a catalyst bed length of approximately 16". The volume of catalyst charged to each reactor was approximately 200 cc (loose). Temperatures were continuously recorded by means of a thermocouple situated at the center of each catalyst bed. Heat was supplied to the reactor by means of an electrically heated lead bath.

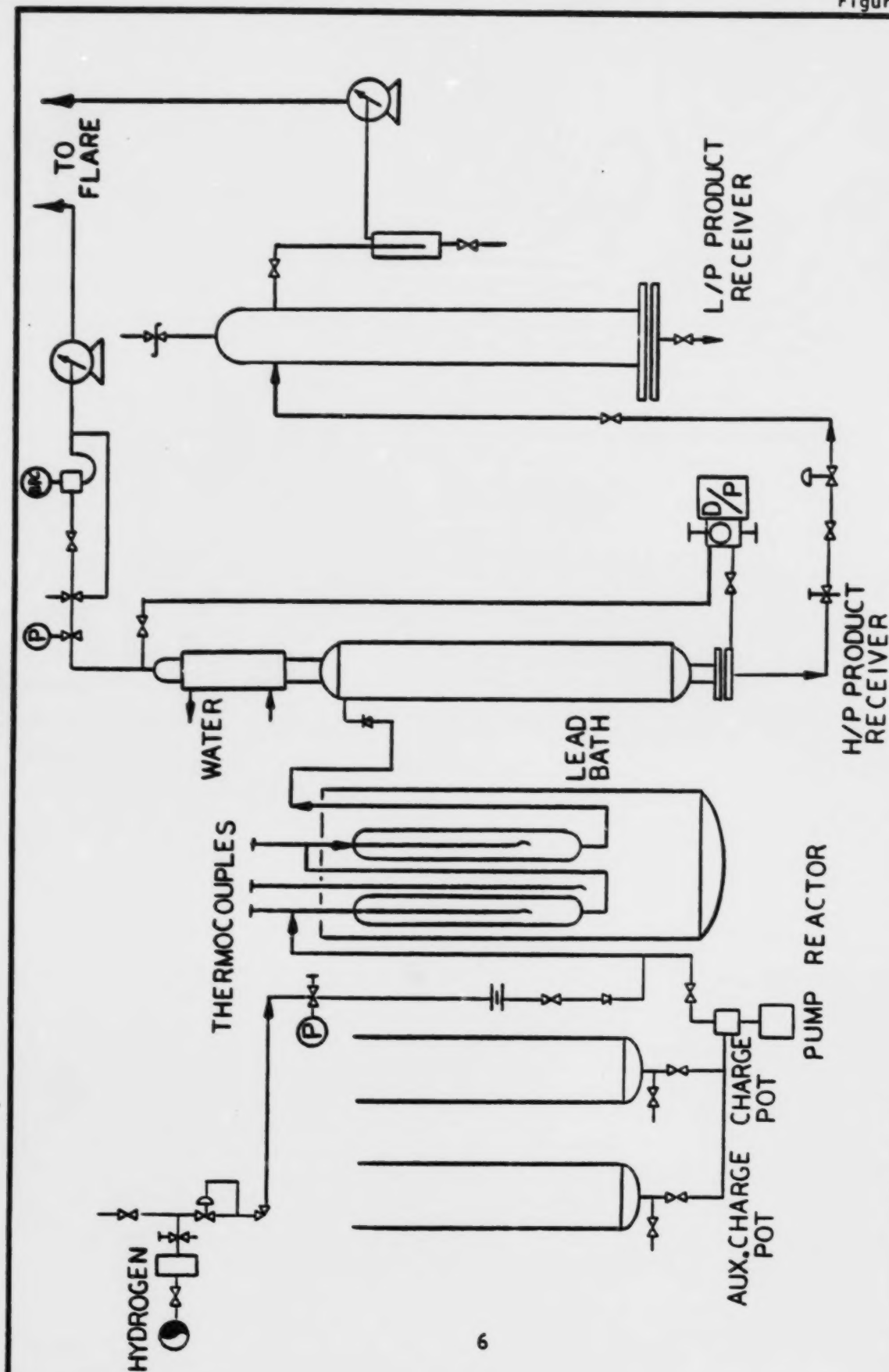
The reason two reactors were connected in series, was to increase production of demetallized product for subsequent desulfurization runs, while maintaining normal liquid space velocities for catalyst deactivation studies. A standard startup procedure was used to condition the catalyst at lower temperatures for a short period of time. The startup schedule was as follows:

Period	----- 1A -----			1B, 2, Etc.
Temperature	750	775	790	790
Pressure, psig	2000	2000	2000	2000
Hydrogen Rate, SCF/Bbl	4000	4000	4000	4000
Liquid Space Velocity, Vo/Hr/Vr	----- Constant -----			
Time on Temp., Hrs.	4	4	1	Continue at above conditions

All demetallization runs in this series were carried out at 790°F except one which was at 770°F. In that one case the final temperature was not exceeded in the startup procedure. Liquid space velocities varied from 0.25 to 2.0 Vo/Hr/Vr.

The melted charge stock was pumped to reactor pressure with a metering pump, mixed with hydrogen makeup gas, and fed to the top of the reactor. The hydrogen concentration of the makeup gas was 100% and no recycle of the exit gases was employed. The mixed vapor and liquid product from the reactors was cooled and passed to a high pressure receiver from which gas was

FIGURE 1



HYDROCARBON RESEARCH, INC.
a subsidiary of
DYNALUTION CORPORATION

REFER. AF-2552

FIXED BED
DEMETALLIZATION UNIT

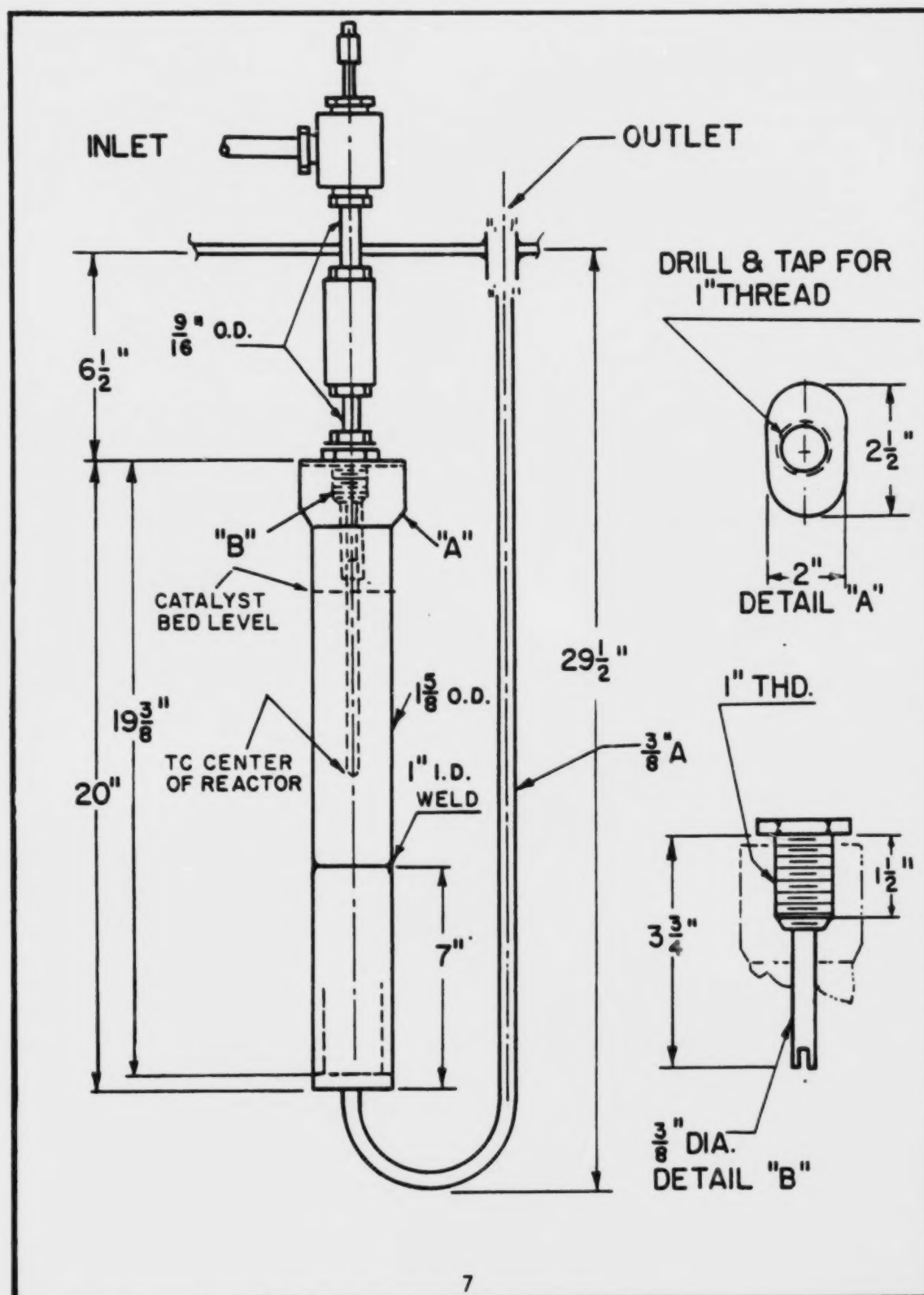
DESIGNED BY: NEAL P. DATE: 2-16-76

ENGINEER: DATE:

PROCESS NO. AF-2681

Figure 2. FIXED BED DEMETALLIZATION REACTOR

Figure 2



sampled, metered, and vented. The net product was let down in pressure and passed to a low pressure receiver from which gas was sampled periodically, metered, and vented. The gases were analyzed twice weekly on a mass spectrometer, Du Pont Model 21-103C. The liquid product was collected and weighed periodically. Daily inspections of the liquid product included; gravity by hydrometer, atmospheric distillation to 550°F, sulfur analysis on the 550°F+ fraction by Leco induction furnace method ASTM-D-1552, and metals analysis for vanadium and nickel by atomic absorption Perkin Elmer Model 303. Besides the daily inspections, about twice weekly and after a change in operating condition, sulfurs were analyzed on the initial to 550°F fraction, and appropriate corrections made on total product sulfurs.

Detailed operating conditions and liquid product inspections for each run in this series is given in Appendix A.

Upon completion of a run, the catalyst was removed from each reactor and analyzed. First the oil was removed from the catalyst by means of a Soxhlet extractor using benzene, then analyzed for carbon, sulfur, vanadium and nickel.

Metals and sulfurs were analyzed using the same equipment as for liquid products while carbon was analyzed by high temperature combustion in oxygen using Perkin Elmer Model 240 C H N analyzer. Pore size distribution curves were obtained by mercury intrusion on Aminco's 60,000 PSI Porosimeter.

3.2 Catalyst Description and Inspections

The catalyst used in all demetallization runs was a representative portion from the 10,000 pound commercial production run made by Minerals and Chemical Division of Engelhard Corporation, and designated HRI 3634. This catalyst, activated bauxite impregnated with one weight per cent molybdenum, was developed by HRI under Phase I of the current contract and produced and evaluated under Phase II. Table 1 lists the physical and chemical characteristics and Figure 3 the pore size distribution of the catalyst.

3.3 Bachaquero Export Vacuum Residuum; Preparation and Inspections

The feed selected for this study was Bachaquero Export Vacuum Residuum. This feed originated in the Lake Maracaibo area of Venezuela. In 1974, the total production of this crude was about

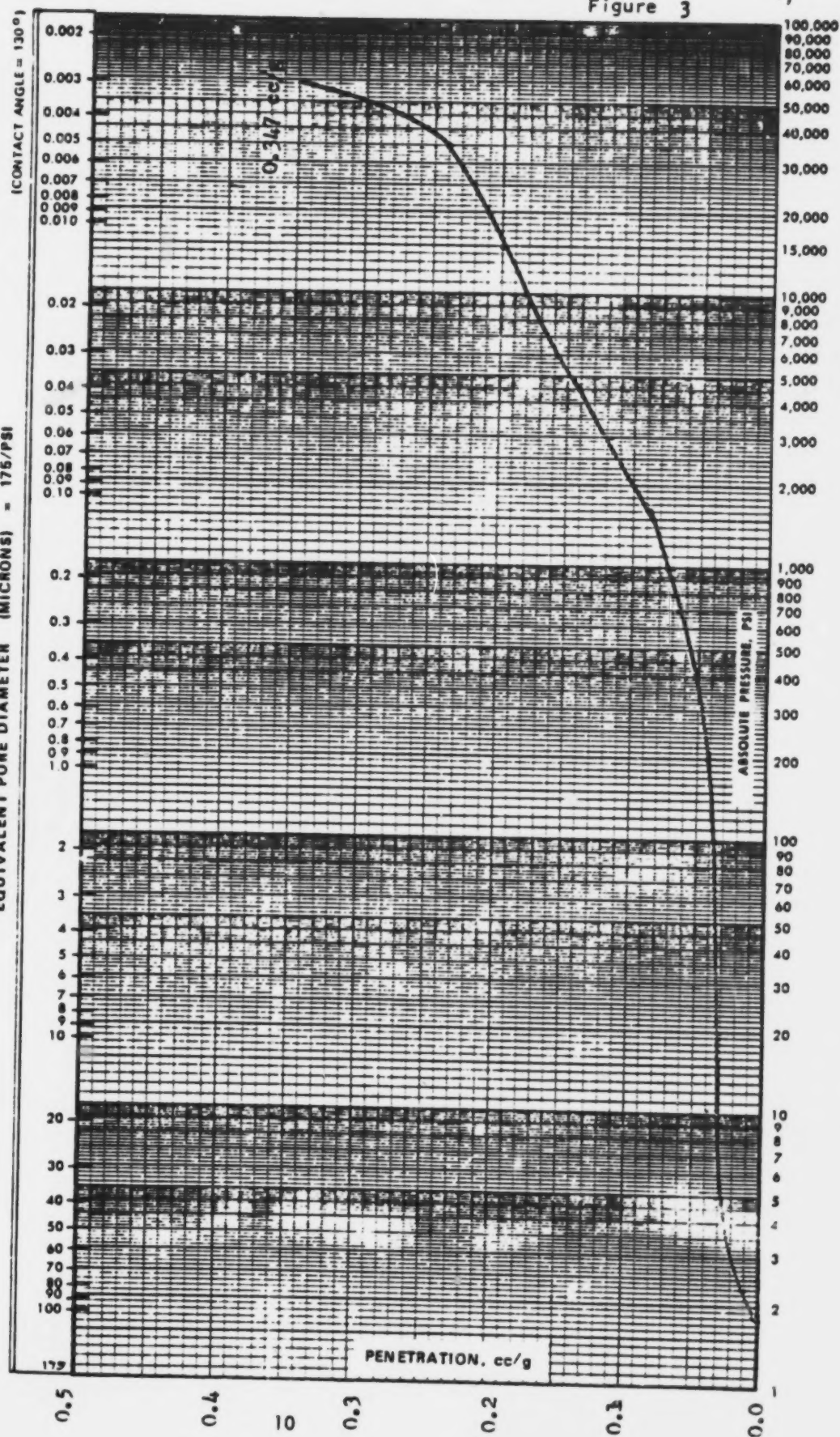
Table 1. DEMETALLIZATION CATALYST INSPECTIONS

HRI Identification Number	3634
Size	20 x 50 U.S. Mesh
Molybdenum, W %	1.06
Volatile Matter, W %	2.0
Bulk Density, g/cc	1.01
Surface Area, M ² /g	195.6
Pore Volume, cc/g	0.347
<u>Sieve Analysis, W %</u>	
20/30 Mesh	52.4
30/40 Mesh	30.7
40/50 Mesh	16.9

Figure 3. DEHETALLIZATION CATALYST HRI 3634

PORE SIZE DISTRIBUTION

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI



204 million barrels equivalent to about 98 million barrels of vacuum residuum (based on a typical 48 percent by volume of 950°F+ resid on crude), with an estimated crude reserve of about 1837 million barrels. The vacuum residuum used for the three levels of demetallization runs was prepared by vacuum distilling Bachaquero Export atmospheric residuum obtained from the Amuay Refinery of Creole Petroleum Corporation, a subsidiary of Exxon Corporation. Three drums of approximately 400 pounds each of vacuum residuum were recovered from 6.5 drums of atmospheric residuum. Inspections on this material designated as HRI L-397 are given in Table 2.

These inspections are somewhat different from published values for pure Bachaquero vacuum residua. Residua designated as "Export" in general contain small quantities of residua from different crudes from a refinery run. The refinery at Amuay obtains its crude from the Lake Maracaibo field in Venezuela through a pipeline. This field is a continuous field comprising Bachaquero, Lagunillas, and Tia Juana crudes, among others.

The Bachaquero Export atmospheric residuum shipped and used for this study contains unknown quantities of residua from these other crudes but is representative of residual oils from this major field available for world markets

3.3.1 Low Level Demetallization

The objective of this operation was to demetallize Bachaquero Export vacuum residuum to 45-50 percent vanadium removal level, produce sufficient feed for a subsequent 20 day desulfurization run, and obtain catalyst deactivation data.

The operation was carried out in Run 115-1233 at 790°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.5 Vo/Hr/Vr and catalyst space velocity of 0.114 Bbl/D/Lb. The actual demetallization achieved was 44 percent vanadium removal and 35 percent desulfurization. Six days of operation produced sufficient feed for a 20 day desulfurization run.

Figure 4 shows the rate of vanadium removal, V_F/V_P , (vanadium in the feed/vanadium in the product) against catalyst age in Bbl/Lb. These results show that, at this level of vanadium removal, the catalyst deactivation is quite low. Desulfurization data obtained from this operation are summarized in Figure 5.

Table 2. FEEDSTOCK INSPECTIONS

Feedstock	Bachaquero Export Vacuum Residuum
HRI Identification No.	L-397
Gravity, °API	7.6
Sulfur, W %	3.08
RCR, W %	17.9
Carbon, W %	86.28
Hydrogen, W %	10.67
Nitrogen, ppm	5313
Vanadium, ppm	577
Nickel, ppm	81
Viscosity, SFS @ 210°F	1945
SUS @ 210°F	118
IBP-975°F, V %	10.0
Gravity, °API	20.3
Sulfur, W %	2.62
975°F+, V %	90.0
Gravity, °API	6.6
Sulfur, W %	3.10
RCR, W %	22.0

Figure 4. DEMETALLIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM

OVER 1.0 W % MOLYBDENUM/20x50 MESH BAUXITE

Feed Composition

Gravity, °API 7.5 to 7.6
Sulfur, W % 2.95 - 3.08
Vanadium, ppm 547
Nickel, ppm 74

Catalyst HRI No. 3634

Legend

Run No.

Operating Conditions

Hydrogen Pressure, psig

Temperature, °F

Liquid Space Velocity, V/HR/V

Catalyst Space Velocity, B/D/LB

Demetallization	
Low Level A	Medium Level B
115-1233	115-1238
2000	2000
790	790
1.5	0.5
0.114	0.037

VANADIUM IN FEED/VANADIUM IN PRODUCT

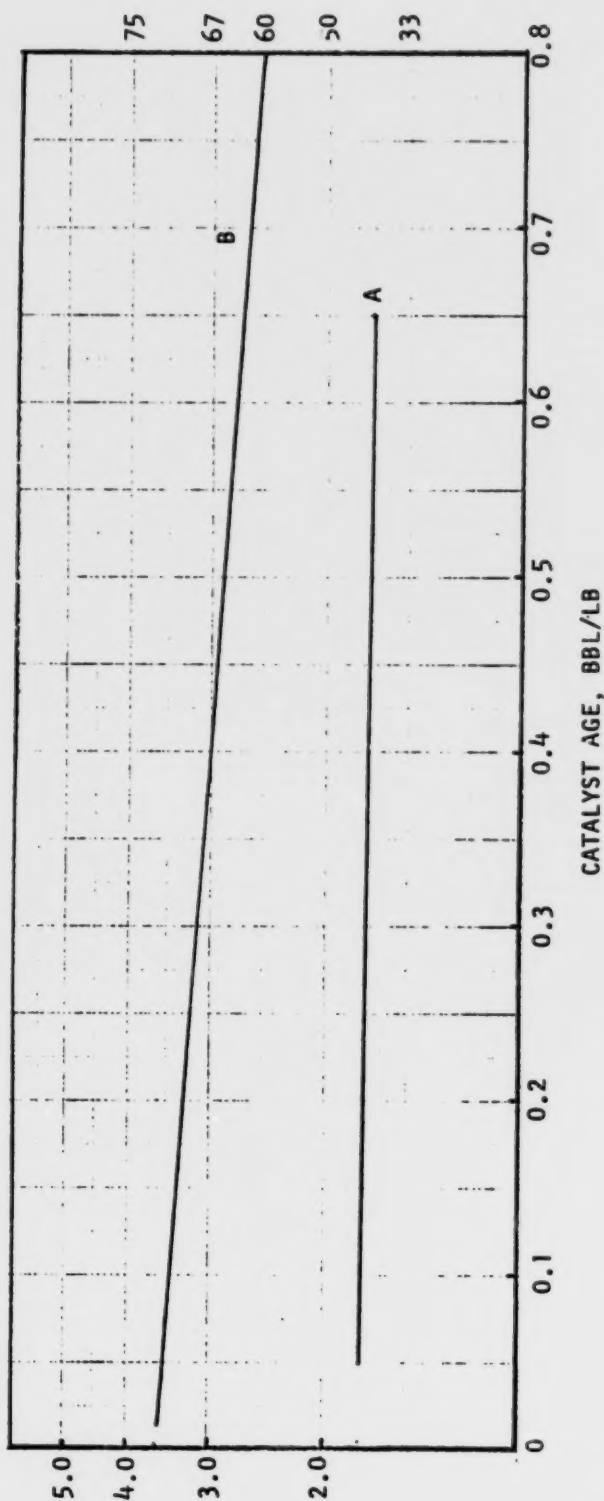


Figure 4

Figure 5. DESULFURIZATION OBTAINED DURING DEMETALLIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM

OVER 1.0 W % MOLYBDENUM/20x50 MESH BAUXITE

Feed Composition

Gravity, °API 7.5 to 7.6
Sulfur, W % 2.95 - 3.08
Vanadium, ppm 547
Nickel, ppm 74

Catalyst HRI No. 3634

Legend

Run No.

Operating Conditions

Hydrogen Pressure, psig

Temperature, °F

Liquid Space Velocity, V/HR/V

Catalyst, Space Velocity, B/D/LB

Demetallization

Low Level Medium Level
A B

115-1233 115-1238

2000 2000

790 790

1.5 0.5

0.114 0.037

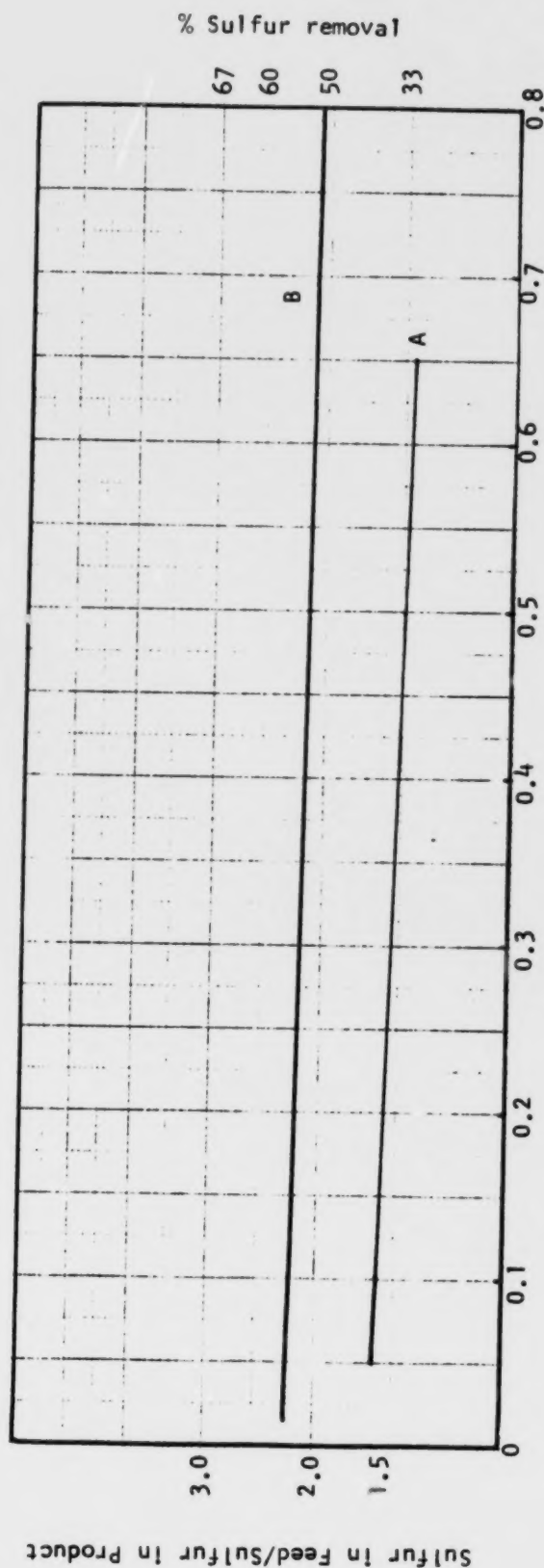


Figure 5

3.3.2 Medium Level Demetallization

The objective of this operation was to demetallize Bachaquero Export vacuum residuum to 65-70 percent vanadium removal level, produce sufficient feed for three desulfurization runs of 20 days each, and obtain catalyst deactivation data.

This operation was carried out in Run 115-1238 at 790°F, hydrogen pressure of 2000 psig, liquid space velocity of 0.5 Vo/Hr/Vr and catalyst space velocity of 0.037 Bbl/D/Lb. The initial vanadium removal rate was 70 percent which fell to 67 percent after 10 days, corresponding to a catalyst age of 0.36 Bbl/Lb. When the vanadium removal rate reached 60 percent after 20 days, corresponding to a catalyst age of 0.76 Bbl/Lb, the run was terminated. The average demetallization achieved during this run was 67 percent vanadium removal and 53 percent desulfurization.

The catalyst deactivation rate is shown in Figure 4 along with results from the low level demetallization operation. Desulfurization data obtained during this operation are given in Figure 5. Indications are that catalyst deactivation rates are strongly dependent on the level of vanadium removal. The catalyst deactivation slope from the low level demetallization operation (47 percent initial vanadium removal) was 0.11, but when the demetallization level was increased to 70 percent initial vanadium removal, the catalyst deactivation slope increased four-fold to 0.44. This rapid deactivation of the catalyst may limit the severity at which Bachaquero Export vacuum residuum can be demetallized over this catalyst.

This one medium level demetallization run produced insufficient feed to sustain three 20 day desulfurization runs. Consequently, a second run was started as Run 115-1239 under identical conditions. Demetallization and desulfurization from this operation are summarized in Figure 6. Initial demetallization and up to catalyst age of 0.1 Bbl/Lb was 74 percent vanadium removal. There was a sudden drop to 54 percent vanadium removal which gradually increased to 62 percent at catalyst age 0.5 Bbl/Lb. At this time, the feed rate was reduced from 0.5 to 0.35 Vo/Hr/Vr. This change resulted in improved demetallization to about 70 percent vanadium removal level. However, after catalyst age of 0.65 Bbl/Lb, the vanadium level again dropped unexpectedly to 50 percent. For this reason the run was terminated, the catalyst removed and analyzed. Visual inspection revealed no abnormalities in the reactors, catalyst, or product lines. Analysis of the used catalysts, (tabulated in Table 4 at the end of the demetallization section) showed the carbon level to be higher in the second reactor from this run than the corresponding reactor from the first run. This indicated that some coking may have

Figure 6 DEMETALLIZATION AND DESULFURIZATION OBTAINED DURING DEMETALLIZATION OF

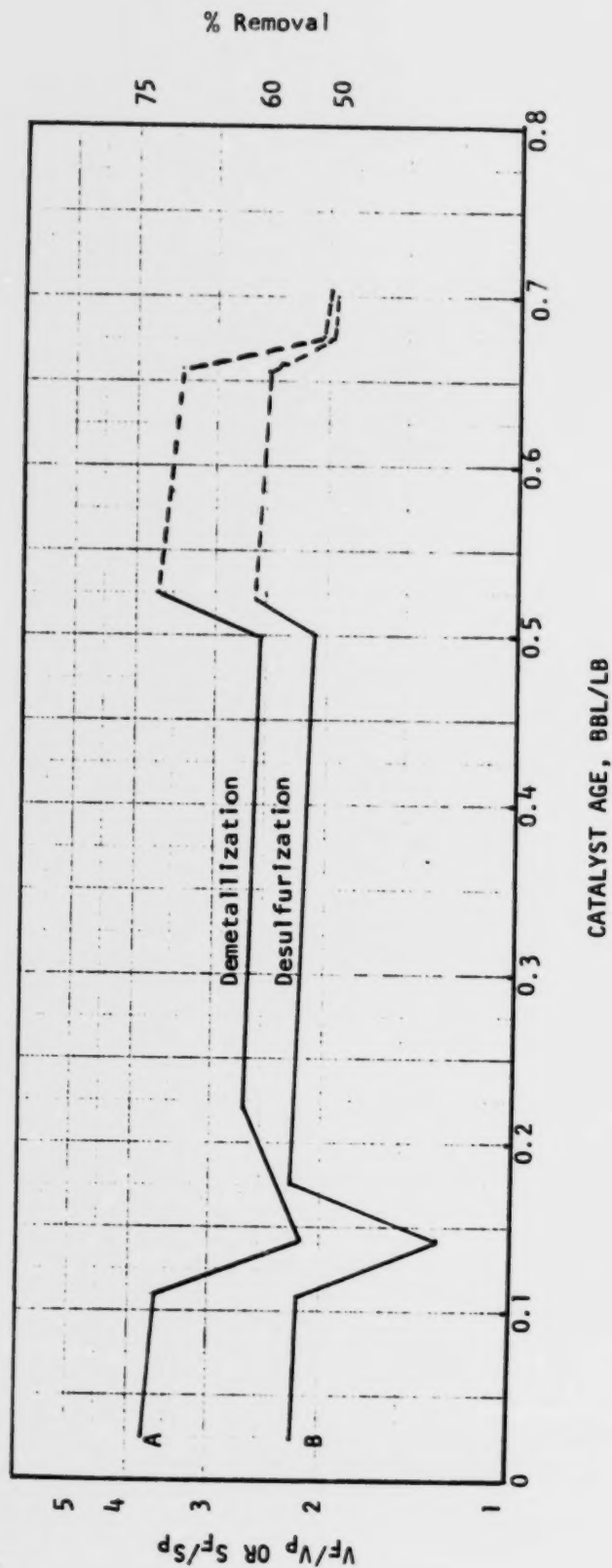
BACHAQUERO EXPORT VACUUM RESIDUUM OVER 1.0 W & MOLYBDENUM/20x50 MESH BAUXITE

Feed Composition: 7.3 °API, 3.0 % S, 577 ppm V, 81 ppm Ni

Symbol	Run No.	Hydrogen Pressure psig	Temp °F	Liquid Space Velocity V/Hr/V	Catalyst Space Velocity B/D/LB
—	115-1239	2000	790	0.5	0.038
----	115-1239	2000	790	0.35	0.027

A V_F/V_p , Vanadium in Feed/Vanadium in Product

B S_F/S_p , Sulfur in Feed/Sulfur in Product



occurred during the course of the second run. Since no difficulty was encountered in the first run under identical conditions, it was inferred that either the liquid feed and/or the hydrogen flow was interrupted during the course of the run. This condition may have existed for too short a period of time to be noted and logged on the daily log sheet.

3.3.3 High Level Demetallization

The objective of the high level demetallization operation was to demetallize Bachaquero Export vacuum residuum to 80-85 percent vanadium removal level, produce sufficient feed for a 20 day desulfurization run, and obtain catalyst deactivation data.

In all, five runs were required to produce sufficient feed for a 20 day desulfurization run. The first four runs were made at 790°F, hydrogen pressure of 2000 psig, liquid space velocity of 0.3 Vo/Hr/Vr and catalyst space velocity 0.023 Bbl/D/Lb.

The first run (115-1240) operated for nine days, at which time pressure buildup in the unit forced a premature shutdown. Average demetallization achieved was 84 percent vanadium removal and 69 percent desulfurization. Although catalyst dumped from the reactor was free-flowing, carbon level on catalyst from the second reactor was unusually high (17.62 W %), indicating coking had occurred during the course of the run.

The second run (115-1241) operated for five days before pressure buildup forced termination of the run. Average demetallization was 85 percent vanadium removal and 67 percent desulfurization. Carbon level on catalyst from second reactor was 15.62 weight percent.

The third run (115-1242) operated for five days before pressure buildup was encountered. An attempt was made to save the run by flushing the reactors with light oil, which restored normal pressure drop. However, on restarting the unit, vanadium removal was sharply reduced and the run had to be terminated. The average demetallization achieved during the first five days of operation was 85 percent vanadium removal and 69 percent desulfurization. Carbon levels on the catalyst were again unusually high indicating coking. It was believed at this time that coking was due to interruption of either feed or hydrogen flow at some time during the run because of difficulty in controlling the very low flow rates used, rather than the severity of the operating conditions.

After again changing the hydrogen metering orifice and clearing

product line and check valve, a fourth run (115-1243) was started. Pressure buildup was encountered after four days, forcing a shut-down. Demetallization was 84 percent vanadium removal and 67 percent desulfurization. Carbon levels were very high on catalysts from both reactors; 21.43 weight percent on catalyst from bottom of first reactor and 19.69 weight percent from the second reactor.

The fifth run (115-1244) was carried out at a lower temperature (770°F) and lower liquid space velocity (0.25 $V_o/Hr/V_r$). The initial vanadium removal was 79 percent dropping to 75 percent after six days on stream. At this time, the temperature was raised to 780°F which restored the vanadium removal level to 79 percent. After eight days on stream, this run was voluntarily terminated because sufficient demetallized product had been accumulated to make a 20 day desulfurization run. Since no evidence of coking was experienced during the course of the fifth run, the conclusion was that in this equipment and at the very low liquid space velocities used, 790°F reactor temperature is above the threshold of coking on this feedstock.

Figure 7 shows the catalyst deactivation plots of the five high level demetallization runs. The first four runs (115-1240, 1241, 1242, and 1243) are reproducible and show a rapid rate of deactivation. The fifth run (115-1244) operated at a lower temperature (770 and 780°F) and slightly lower liquid space velocity, showed a lower rate of deactivation.

Sulfur removal and nickel removal as function of vanadium removal are summarized in Figure 8.

It can be concluded from the results of the high level demetallization operation that:

1. High levels of demetallization, up to about 80 percent vanadium removal, can be achieved on Bachaquero Export vacuum residuum over the newly developed catalyst. However, deactivation slope of the catalyst was high.
2. In this equipment temperatures above about 780°F combined with very low liquid space velocities, below about 0.25 $V_o/Hr/V_r$ may pose operability problems because of coking. At high reaction rates, hot spots in the reactor which were not recorded, may have been the cause of the coking in our test unit. However, run away temperatures in commercial equipment can be prevented where

Figure 7. DEMETALLIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM

OVER 1.0 W % MOLYBDENUM/20x50 MESH BAUXITE

Feed Composition: 7.3 °API, 3.0 % S, 577 ppm V, 81 ppm Ni

Legend	Run No.	Hydrogen Pressure psiq	Temp. °F	V/HR/V	B/D/LB
▲	115-1240	2000	790	0.30	0.023
●	115-1241	2000	790	0.30	0.023
○	115-1242	2000	790	0.30	0.023
■	115-1243	2000	790	0.30	0.023
▲	115-1244	2000	780	0.25	0.019
△	115-1244	2000	770	0.25	0.019

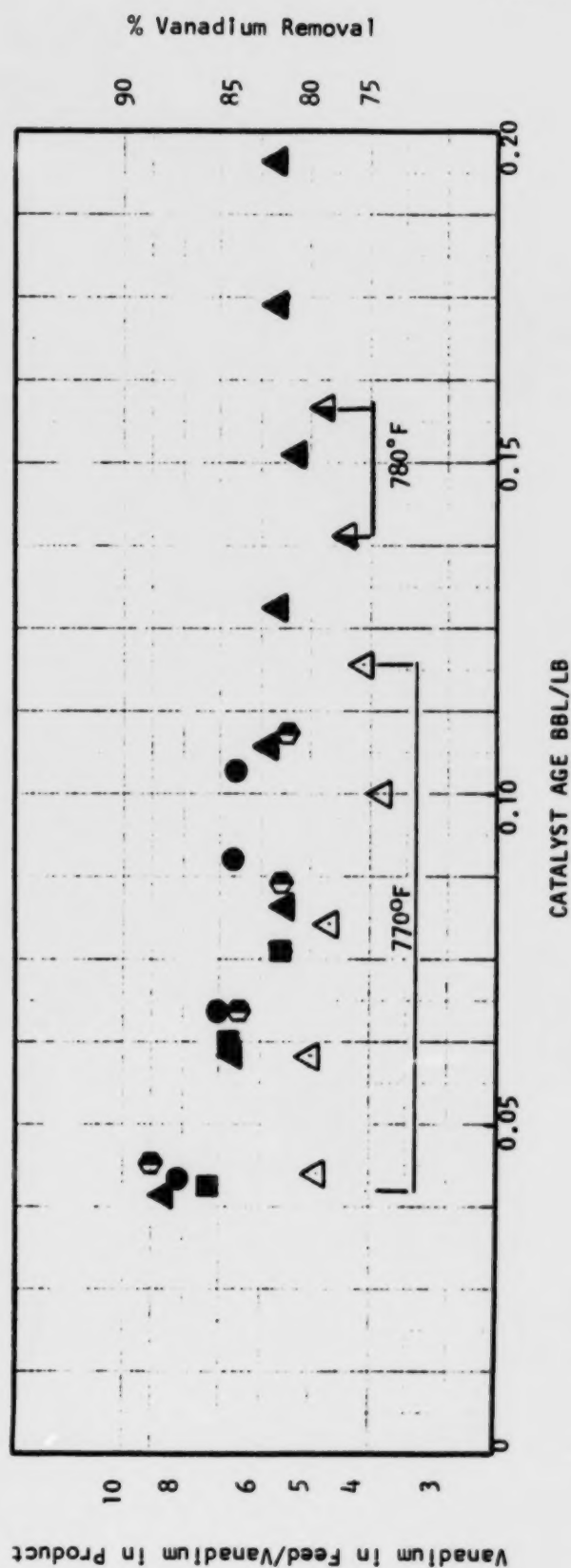
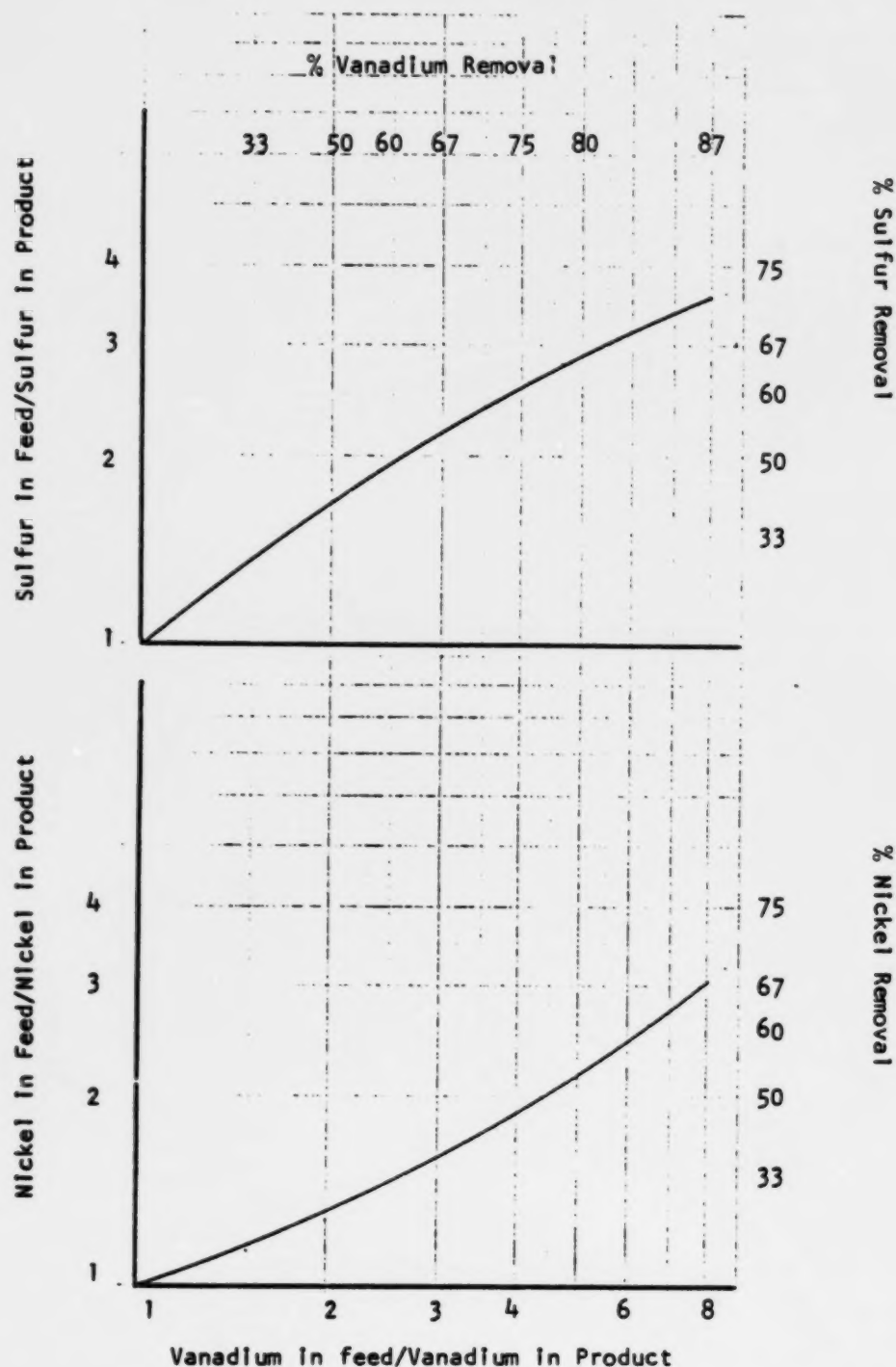


Figure 7

Figure 8

Figure 8. SULFUR AND NICKEL REMOVALS AS FUNCTION OF VANADIUM REMOVAL
DURING DEMETALLIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM

ON 1 % MOLYBDENUM/20x50 MESH BAUXITE



quenching is normally practiced.

3. Catalyst deactivation rates increase sharply with demetallization operations above 70 percent vanadium removal.

3.4 Lloydminster Vacuum Residuum; Preparation and Inspections

Lloydminster crude originates in Western Canada in the provinces of Alberta and Saskatchewan. In 1975, the daily production rate of this crude was 33,000 barrels per day which corresponds to a yearly production of about 12 million barrels. The equivalent production of the vacuum residuum was about 6.6 million barrels.

The Lloydminster vacuum residuum used in this program was obtained from Husky Oil Ltd., Lloydminster, Alberta. This feed is high in sulfur content (5.4 % S) and contains moderate amounts of vanadium and nickel. Detailed inspections on this feed are give in Table 3.

3.4.1 Demetallization to 45-60 Percent Vanadium Removal

The objective of this operation was to demetallize Lloydminster vacuum residuum to 45-60 percent vanadium removal, produce sufficient demetallized feed for a subsequent desulfurization run to last about 30 days and obtain catalyst deactivation data.

This operation was carried out in Run 115-1248 at 790°F, hydrogen pressure of 2000 psig, liquid space velocity of 2.0 Vo/Hr/Vr and catalyst space velocity of 0.15 Bbl/D/Lb. The run was started at a liquid space velocity of 1.5 Vo/Hr/Vr which resulted in 73 percent vanadium removal, higher than the intended demetallization level. The liquid space velocity was increased to 2.0 Vo/Hr/Vr after two days, lowering the demetallization level to 64 percent vanadium removal. The run was continued for nine days at the higher feed rate, at which time the run was voluntarily terminated because sufficient feed had been accumulated for the desulfurization run.

Figure 9 shows the catalyst deactivation with age and Figure 10 shows the desulfurization achieved during this operation. The average demetallization was 61 percent vanadium removal and average desulfurization was 50 percent.

Table 3. FEEDSTOCK INSPECTION

Feedstock	Lloydminster Vacuum Residuum
HRI Identification No.	3744
Gravity, °API	6.4
Sulfur, W %	5.40
RCR, W %	15.8
Nitrogen, ppm	5900
Carbon, W %	83.18
Hydrogen, W %	10.37
Vanadium, ppm	164
Nickel, ppm	95
Viscosity, SFS @ 210°F	1489
IBP-975°F, V %	20.9
Gravity, °API	17.0
Sulfur, W %	3.49
975°F+, V %	79.1
Gravity, °API	3.1
Sulfur, W %	5.88
RCR, W %	20.8

Figure 9 DENETALLIZATION OF LLOYDMINSTER VACUUM RESIDUUM

OVER 1 W % MOLYBDENUM/20x50 MESH BAUXITE

HRI No. 3634

Feed Composition: 6.4 °API, 5.4 % Sulfur, 169 ppm V, 95 ppm NI
HRI 3744

Symbol	Run No.	Hydrogen Pressure psig	Temperature °F	V/Hr/V	B/D/Lb.	Data Corrected To V/Hr/V	B/D/Lb.
A	115-1248	2000	790	1.5-2.0	0.112-0.15	2.0	0.15
B	115-1249	2000	790	0.62-0.77	0.048-0.059	0.65	0.05

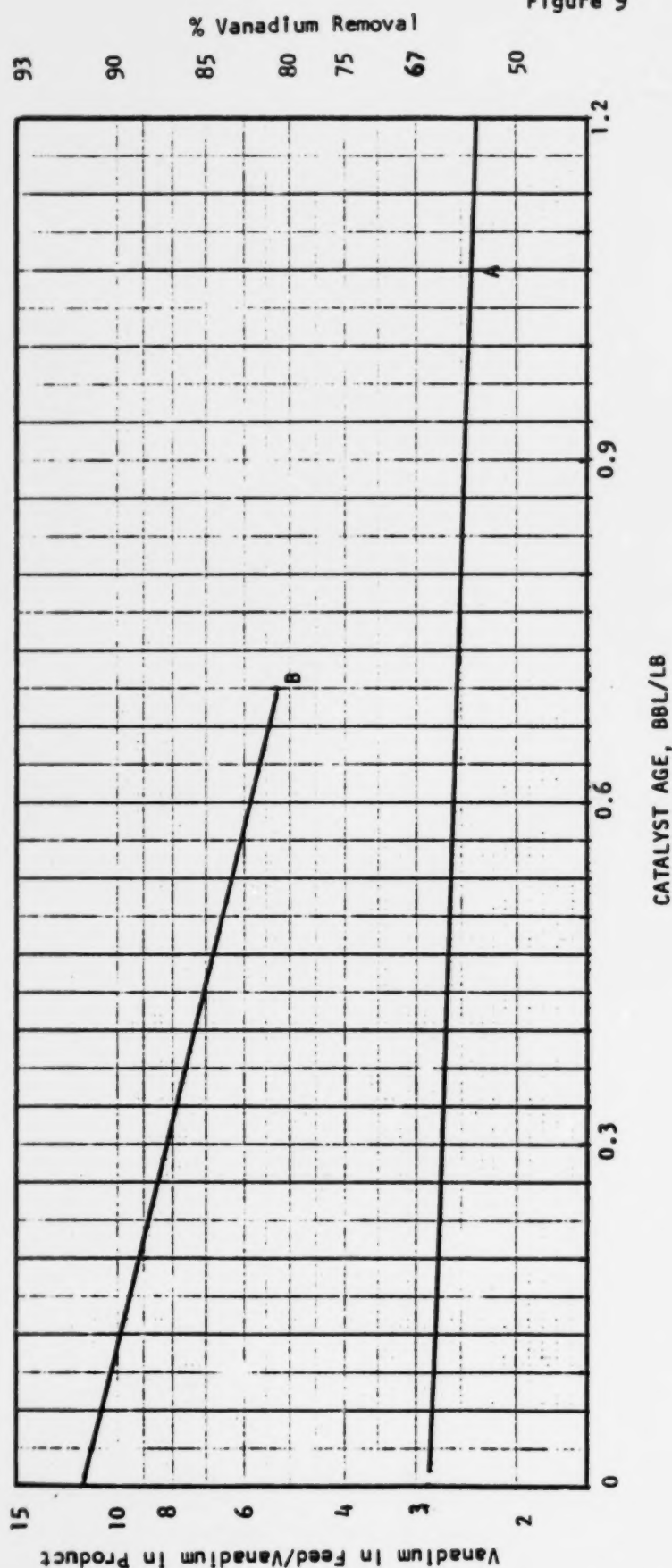


Figure 9

Figure 10 DESULFURIZATION OBTAINED DURING DEMETALLIZATION OF LLOYDMINSTER VACUUM RESIDUUM

OVER 1 W % MOLYBDENUM/20x50 MESH BAUXITE

HRI 3634

Feed Composition: 6.4 °API, 5.4 % S, 169 ppm V, 95 ppm NI
HRI 3744

Symbol	Run No.	Hydrogen Pressure psig	Temperature °F	V/Hr/V	B/D/Lb	Data Corrected to V/Hr/V	B/D/Lb
A	115-1248	2000	790	1.5-2.0	0.15-0.112	2.0	0.15
B	115-1249	2000	790	0.62-0.77	0.048-0.059	0.65	0.05

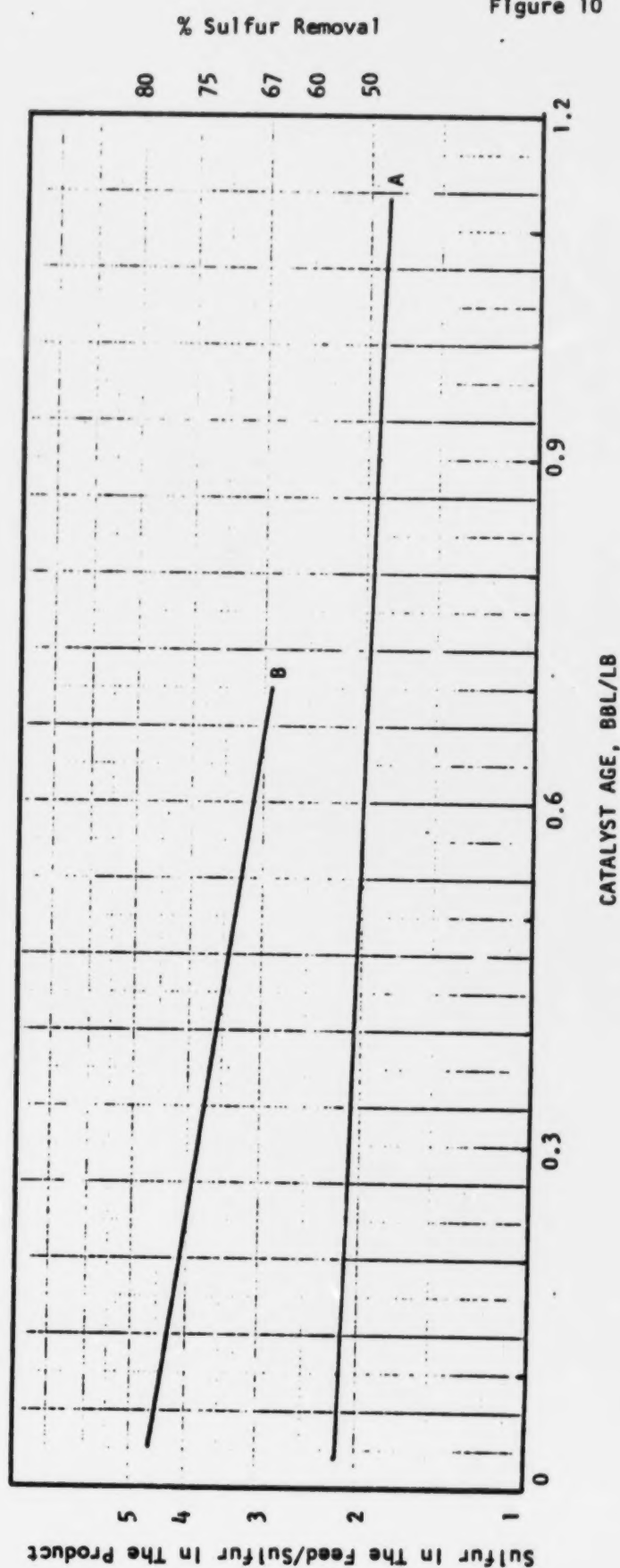


Figure 10

3.4.2 Demetallization to 80-85 Percent Vanadium Removal

Lloydminster vacuum residuum was demetallized to 80-85 percent vanadium removal, sufficient demetallized feed was produced for a 25 day desulfurization run and catalyst deactivation data was obtained.

This operation was carried out in Run 115-1249 at 790°F, hydrogen pressure of 2000 psig, liquid space velocity ranged between 0.52 and 0.80 Vo/Hr/Vr and catalyst space velocity ranged between 0.048 and 0.059 Bbl/D/Lb.

Figure 9 shows the rate of catalyst deactivation with age and Figure 10 shows the desulfurization achieved during this demetallization run.

Initial demetallization was 87 percent vanadium removal which gradually fell to 79 percent after seven days on stream. At this time feed rate was lowered to 0.62 Vo/Hr/Vr restoring the demetallization level to 88 percent. After 13 days on stream the demetallization rate was still at about 82 percent but sufficient feed had been collected for a desulfurization run, so the unit was shut down.

Sulfur removal and nickel removal as function of vanadium removal are summarized in Figure 11.

3.5 Kinetics of Demetallization

Demetallization data obtained on Bachaquero Export vacuum residuum in the liquid space velocity range of 0.3 to 1.5 Vo/Hr/Vr corresponding to catalyst space velocities of 0.023 to 0.114 Bbl/D/Lb were used to develop a kinetic model for vanadium removal over a commercial demetallization catalyst containing 1 percent Molybdenum on 20 x 50 mesh activated bauxite. These data are summarized graphically in Figure 12, showing that the rates of vanadium removal over the given catalyst space velocities follow a pseudo first order kinetics. The kinetic model developed above also fits the data obtained on Lloydminster vacuum residuum over the same demetallization catalyst. These data are included in Figure 12 over the liquid space velocity range 0.65 to 2.0 Vo/Hr/Vr, corresponding to catalyst space velocity range 0.05 to 0.15 Bbl/D/Lb.

The kinetic equation used to correct for variations in space velocities to obtain rate constants for use later in this program

Figure 11

Figure 11. SULFUR AND NICKEL REMOVALS AS FUNCTION OF VANADIUM REMOVAL

DURING DEMETALLIZATION OF LLOYDMINSTER VACUUM RESIDUUM

ON 1 % MOLYBDENUM/20x50 MESH BAUXITE

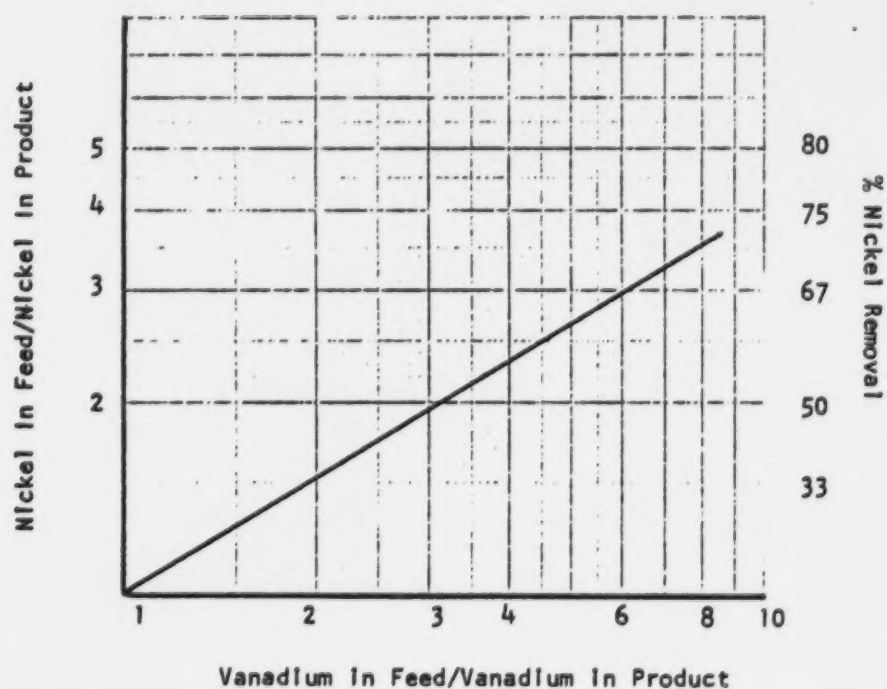
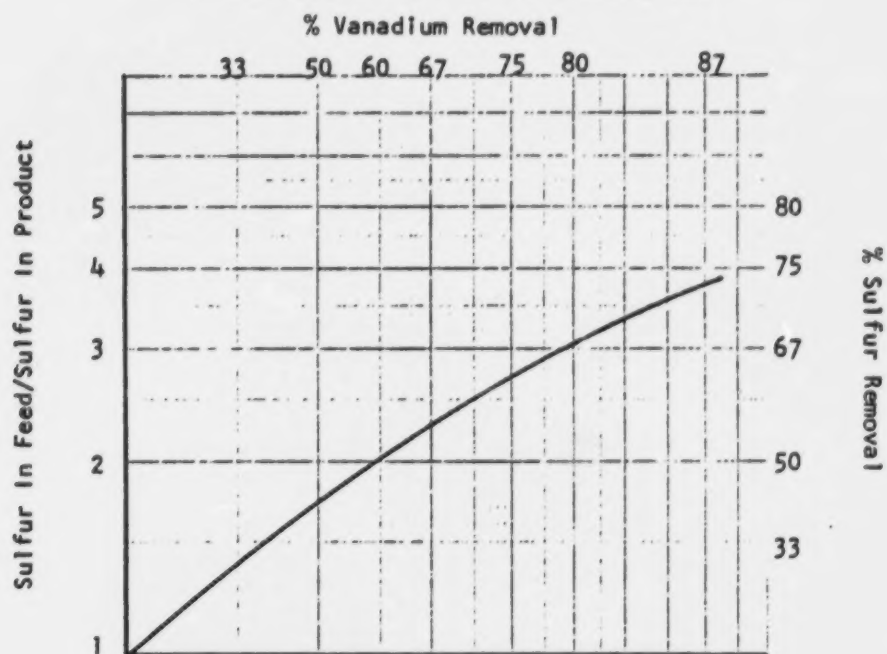


Figure 12. KINETICS OF DEMETALLIZATION

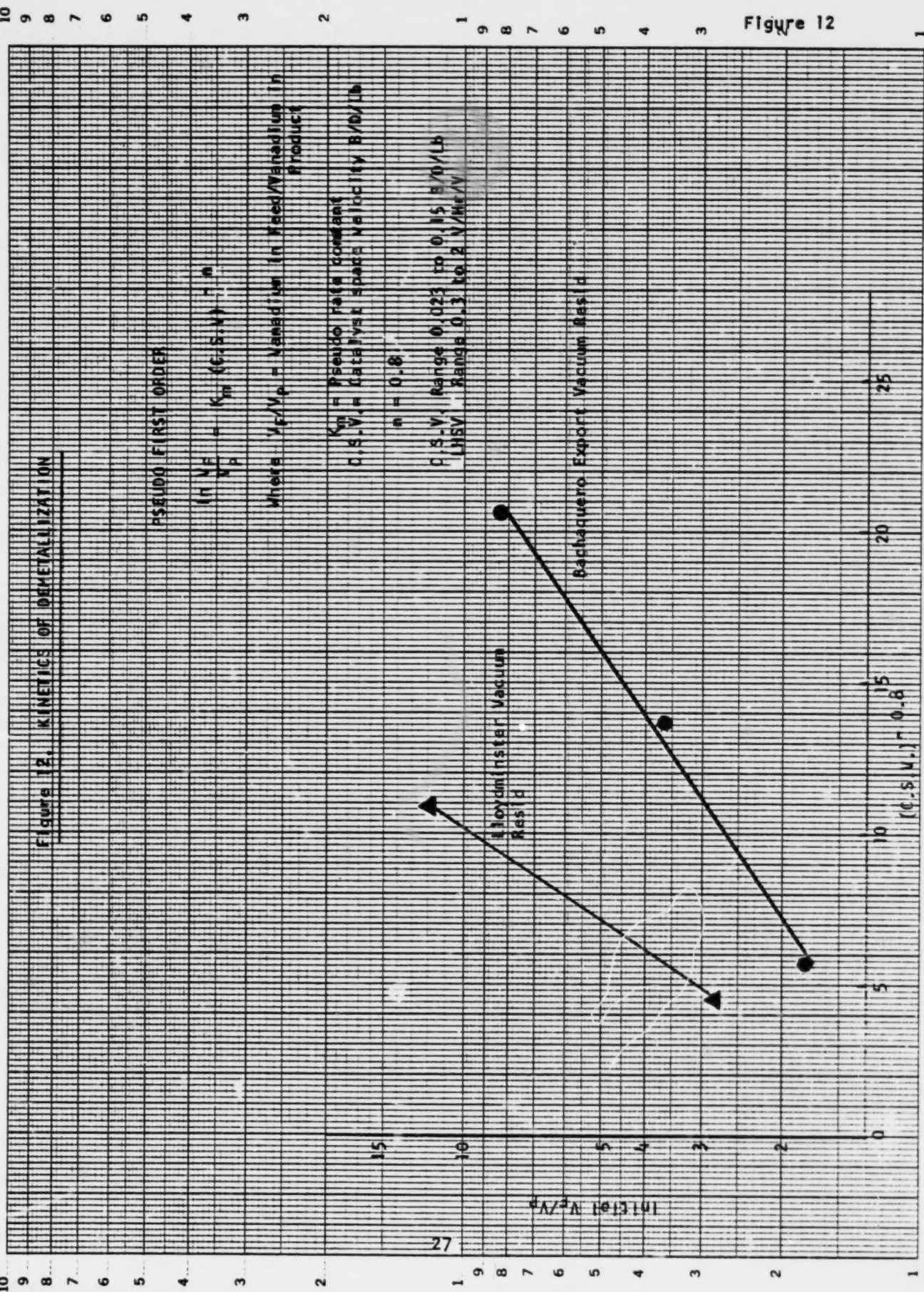


Figure 12

is given in equation (1):

$$K_m = (C.S.V.)^n \ln \frac{V_F}{V_P} \text{ ----- (1)}$$

where K_m = Pseudo First order rate constant

C.S.V. = Catalyst space velocity, Bbl Oil/Day/Lb Catalyst

V_F = Vanadium in feed, in ppm

V_P = Vanadium in product, in ppm

$n = 0.8$

As seen from the slopes of initial rate constants for the two residues in Figure 12, the rate of vanadium removal for Lloydminster vacuum residuum is about twice that for Bachaquero Export. Actual slope for Lloydminster was 0.22, and for Bachaquero Export it was 0.10.

3.6 Spent Demetallization Catalyst Inspections

The results of analyses on spent demetallization catalysts are summarized in Table 4. Carbon levels ranged from about eight weight percent to over 20 weight percent. In all runs where operability problems were encountered with pressure buildup, the carbon level on catalyst was over 15 weight percent while no other operable runs exhibited this high level carbon content. No correlation could be found between carbon level and catalyst age. It appears carbon is deposited rapidly on the catalyst at the beginning of a run, the level being dependent on temperature and liquid space velocity, then remaining fairly constant for the duration of the run. The pore size distribution of the spent demetallization catalyst are summarized in Table 5. The pore volumes of the spent catalysts were corrected to fresh basis using the following relationship:

$$\text{cc/g Fresh Catalyst} = \frac{1}{1.000 - \sum FI + \frac{1}{2} F_s} \times \text{cc/g Spent Catalyst}$$

where FI = weight fraction impurities on spent catalyst

F_s = weight fraction sulfur on spent catalyst

The loss in total pore volume of all demetallization catalysts fell

Table 4. ANALYSES OF SPENT DEMETALLIZATION CATALYSTS

RUN NUMBER	FEED	REACTOR	LHSV $V_o/\text{Hr}/V_r$	CATALYST AGE BBL/LB	CARBON W %	SULFUR W %	VANADIUM W %	NICKEL W %
115-1233	Bachaquero	No. 1	1.50	0.64	8.92	2.56	7.08	0.44
115-1233	Bachaquero	No. 2	1.50	0.64	10.46	2.16	3.44	0.30
115-1238	Bachaquero	No. 1	0.50	0.76	9.32	5.36	12.96	0.81
115-1238	Bachaquero	No. 2	0.50	0.76	12.83	3.51	3.90	0.39
115-1239	Bachaquero	No. 1	0.35-0.50	0.73	9.88	5.58	12.97	0.85
115-1239	Bachaquero	No. 2	0.35-0.50	0.73	15.22	2.86	2.81	0.36
115-1240	Bachaquero	No. 1	0.30	0.20	14.06	2.63	3.43	0.35
115-1240	Bachaquero	No. 2	0.30	0.20	17.62	2.37	1.05	0.16
115-1241	Bachaquero	No. 1	0.30	0.10	13.30	2.38	2.48	0.22
115-1241	Bachaquero	No. 2	0.30	0.10	15.62	2.24	0.69	0.14
115-1242	Bachaquero	No. 1 Top	0.30	0.22	8.45	2.21	8.27	0.41
115-1242	Bachaquero	No. 1 Bottom	0.30	0.22	17.84	2.20	1.20	0.18
115-1242	Bachaquero	No. 2	0.30	0.22	15.37	2.04	1.01	0.17
115-1243	Bachaquero	No. 1 Top	0.30	0.08	14.87	3.09	3.56	0.25
115-1243	Bachaquero	No. 1 Bottom	0.30	0.08	21.43	3.18	0.91	0.12
115-1243	Bachaquero	No. 2	0.30	0.08	19.69	2.56	0.47	0.09
115-1244	Bachaquero	No. 1	0.25	0.15	10.49	2.91	3.60	0.30
115-1244	Bachaquero	No. 2	0.25	0.15	13.77	2.53	0.95	0.15
115-1248	Lloydminster	No. 1	1.50-2.00	1.21	8.03	5.50	5.09	1.72
115-1248	Lloydminster	No. 2	1.50-2.00	1.21	8.01	3.78	2.51	1.10
115-1249	Lloydminster	No. 1	0.62-0.80	0.69	9.50	4.87	4.58	1.92
115-1249	Lloydminster	No. 2	0.62-0.80	0.69	11.40	2.78	1.18	0.64

TABLE 5 PORE SIZE DISTRIBUTION OF SPENT DEMETALLIZATION CATALYSTS

SPENT CATALYST From Run No.	CATALYST AGE Bbl/Lb	WT %		PORE DIAMETER RANGE ANGSTROMS				TOTAL PORE VOLUME cc/gm	LOSS IN TOTAL PORE VOLUME %
		C	V+Ni	30-100	100-500	500-1000	1000+		
				PORE VOLUME	PORE VOLUME	cc/gm			
Fresh 3634				0.142	0.078	0.034	0.057	0.311	
115-1233 R-1	0.64	8.92	7.52	0.039	0.047	0.017	0.034	0.137	55.9
115-1233 R-2	0.64	10.46	3.74	0.034	0.048	0.021	0.044	0.147	52.7
115-1238 R-1	0.76	9.32	13.77	0.021	0.046	0.014	0.035	0.116	62.7
115-1238 R-2	0.76	12.83	4.29	0.027	0.038	0.016	0.043	0.124	60.1
115-1239 R-1	0.73	9.88	13.82	0.031	0.039	0.012	0.042	0.124	60.1
115-1239 R-2	0.73	15.22	3.17	0.021	0.044	0.024	0.041	0.130	58.2
115-1241 R-1	0.10	13.30	2.70	0.030	0.033	0.019	0.042	0.124	60.1
115-1241 R-2	0.10	15.62	0.83	0.021	0.038	0.022	0.043	0.124	60.1
115-1242 R-1 Top	0.22	8.45	8.68	0.029	0.041	0.032	0.037	0.139	55.3
115-1242 R-1 Btm	0.22	17.84	1.38	0.033	0.054	0.014	0.043	0.144	53.7
115-1242 R-2	0.22	15.37	1.18	0.032	0.050	0.019	0.038	0.139	55.3
115-1244 R-1	0.15	10.49	3.90	0.025	0.042	0.021	0.046	0.134	56.9
115-1244 R-2	0.15	13.77	1.10	0.017	0.036	0.020	0.038	0.111	64.3
115-1248 R-1	1.21	8.03	6.81	0.026	0.058	0.024	0.039	0.147	52.7
115-1248 R-2	1.21	8.01	3.61	0.016	0.054	0.026	0.045	0.141	54.7
115-1249 R-1	0.69	9.50	6.50	0.026	0.046	0.015	0.054	0.141	54.7
115-1249 R-2	0.69	11.40	1.82	0.013	0.045	0.024	0.048	0.130	58.2

Note: Pore size distribution and total pore volumes on spent catalysts were corrected to fresh catalyst basis.

into a rather narrow range (53 to 63% loss) considering the large variation in catalyst age (0.1 to 1.21 Bbl/Lb), carbon level (8.0 to 17.8 W %) and metals deposited (0.83 to 13.8 % V & Ni). The greatest loss in pore volume occurred in micropores 30-100 Angstroms in diameter, however no significant correlation could be found between the loss in micropores and the variables catalyst age, carbon or metals level on catalysts.

3.7 Catalyst Deactivation Correlations

The correlation between demetallization level (vanadium removal level) and catalyst deactivation is shown in Figure 13. The data for curve A was obtained from runs made on Bachaquero Export vacuum residuum to produce demetallized feeds containing three levels of vanadium. Data from runs made on Tia Juana (point B) and Gach Saran (point D) vacuum residua, from Phase II work, as well as data from the operation on Lloydminster vacuum residuum (curve C) are included in this Figure.

Curve A indicated that for Bachaquero Export and Tia Juana vacuum residua, vanadium removal above 70 percent will result in rapid catalyst deactivation. The same phenomenon is observed in the case of the Lloydminster feed, but the level of vanadium removal where a sharp increase in deactivation started was about 80 percent. From a single data point on Gach Saran, the corresponding vanadium removal where a sharp increase in deactivation slope occurred is around 88 percent.

The above results also show that the deactivation slope of the catalyst does not depend on the amount of metals in the feed. Demetallization of the lower metals Lloydminster feed resulted in higher deactivation slope than from the corresponding operation on the higher metals Gach Saran feed.

Figure 14 shows the effect of catalyst vanadium loading on the rate constant for Bachaquero and Lloydminster vacuum residua. These results show that the demetallization rate constant depends on the vanadium loading on the catalyst as well as on the level of vanadium removal. For the same level of metals loading on the catalyst, the rate constant for the same feed is higher for the lower level vanadium removal operation. This observation is true for both Lloydminster (lines A and B) and Bachaquero (lines C and D) vacuum residua. However, the effect is lower with Bachaquero feed. For the Bachaquero feed, the variation of the rate constant at medium level (72% initial vanadium removal) and at high level (88% initial vanadium removal) versus vanadium loading on the catalyst (line D) was about the same.

Figure 13

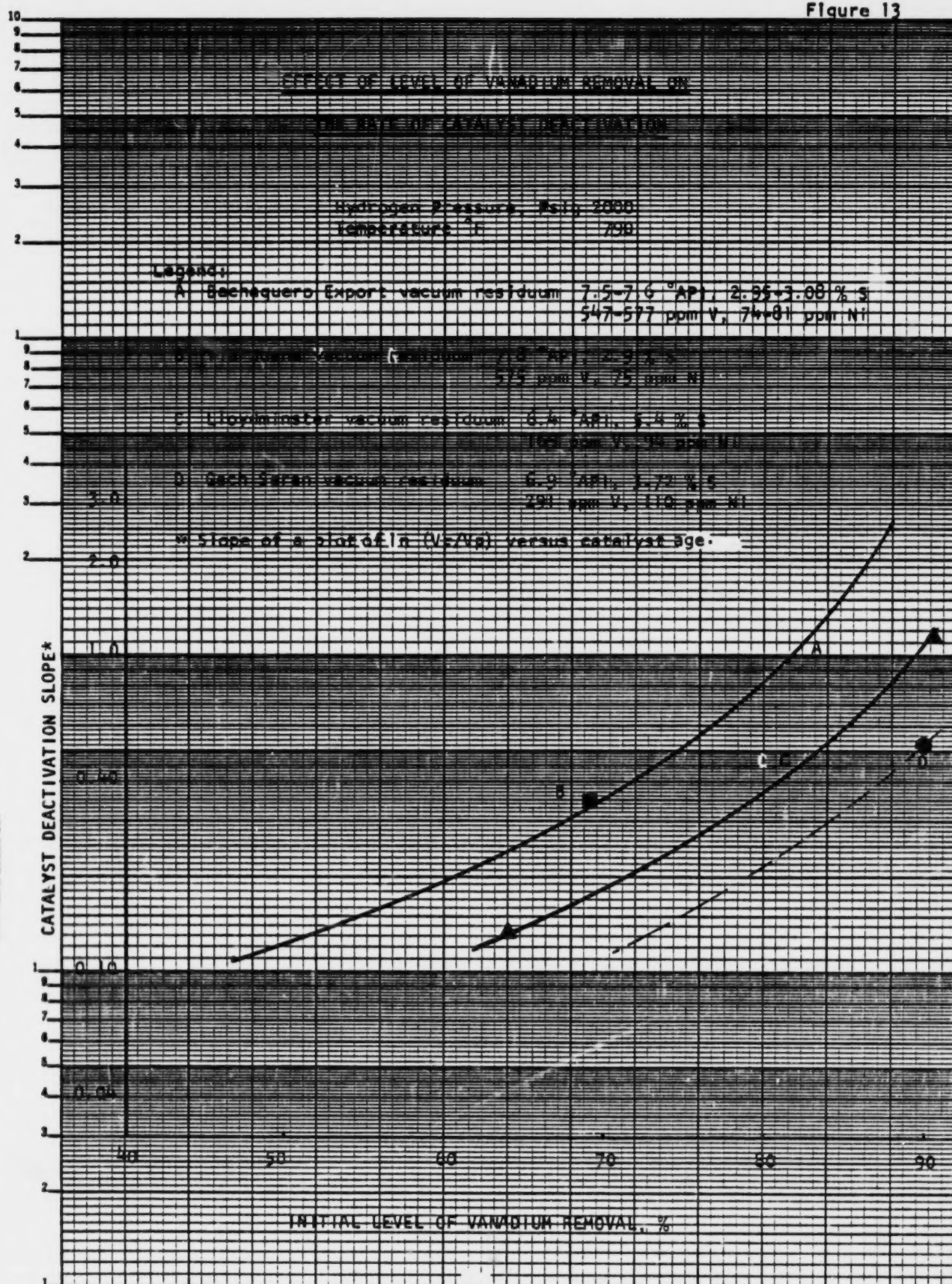
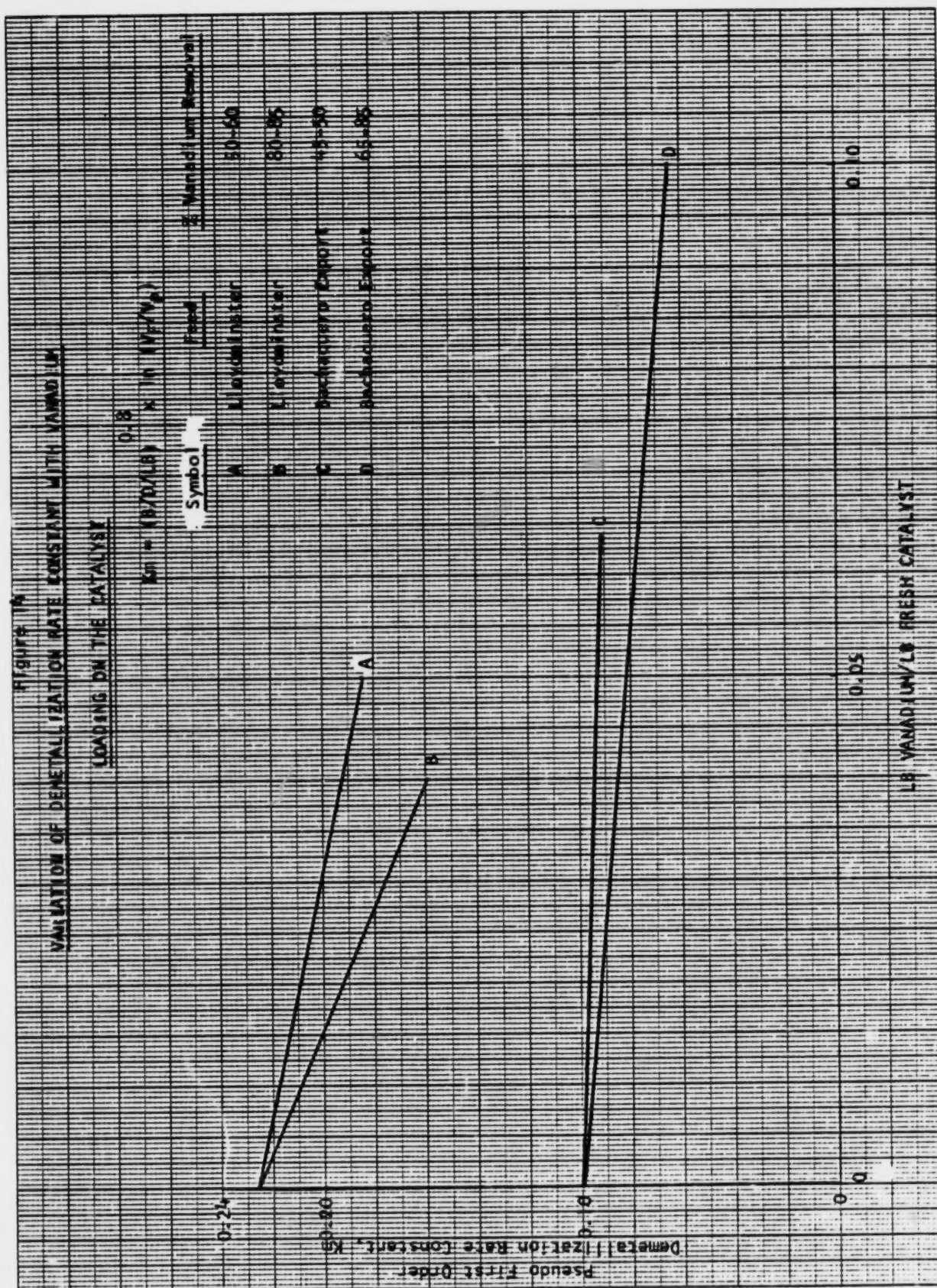


Figure 14



A drop in the value of the demetallization rate constant with increasing metals loading on the catalyst is expected. As the amount of metals deposition on the catalyst is increased the number of active sites is reduced with resulting drop in value of the rate constant.

The change in the value of the demetallization rate constant with level of vanadium removal is believed to be diffusion controlled. At low level vanadium removal operations, metals are removed from smaller molecules which readily diffuse through the pores of the catalyst to the active sites resulting in a high rate constant. At high level vanadium removal operations, metals from larger molecules must be removed which diffuse more slowly to the active sites resulting in lower rate constants.

Based on the above postulation, it appears that the metals containing molecules in Gach Saran feed are smaller than those in Lloydminster feed. Consequently the catalyst deactivation rate is lower for Gach Saran than for Lloydminster feeds at a given vanadium removal level even though Gach Saran has more metals.

The above results indicate that we cannot generalize the effect of metals content of the feed on the deactivation slope of the catalyst, and extrapolation to other feeds should be carried out with caution.

4. EXPERIMENTAL; DESULFURIZATION

The objectives of the desulfurization operations were as follows:

1. Study the effect of metals level in the demetallized feed on the rate of deactivation of the desulfurization catalyst.
2. Study the effect of level of desulfurization on the deactivation rate of the desulfurization catalyst.
3. To determine operating conditions required to produce 0.3 weight percent fuel oil.

4.1 Apparatus and Procedures

All desulfurization operations were carried out in continuous, downflow, fixed bed units 184 and 185. These units are identical to unit 115 shown in Figure 1 except for having a single reactor contained in the lead bath. The reactor shown in Figure 2 was used in all desulfurization runs. In all but three runs full reactor catalyst charge was used (approximately 200 cc loose). In runs 184-196, 197 and 185-248 the volume of catalyst charged to the reactor was approximately 100 cc (loose).

The reduced volume of catalyst charge enabled us to obtain longer catalyst ages, at normal liquid space velocities, using the limited quantities of feedstock available.

The startup and operating procedures used were similar to ones used with the demetallization runs described previously under the demetallization section.

Most of the aging runs were carried out to a catalyst age of 2 to 3 Bbl/Lb. Runs of this duration, together with results from aging desulfurization runs made during Phases I and II of this contract, provide an accurate measure of catalyst deactivation rates which can be translated to the catalyst utilization required to obtain a given product desulfurization level.

Detailed operating conditions and liquid product inspections for each run in this series are given in Appendix B.

4.2 Catalyst Description and Inspections

The catalyst used in all desulfurization runs was high activity

HDS beads obtained from American Cyanamid, designated as HRI 3104. The small size, about 0.02 inch diameter spheres, makes this catalyst particularly resistant to deactivation due to metals deposition, thus making it a likely candidate for use in a commercial process. The properties of the catalyst are summarized in Table 6.

4.3 Demetallized Bachaquero Export Vacuum Residuum

4.3.1 Products from Low Level Demetallization

The demetallized products from Run 115-1233 were blended and designated as HRI L-400. Table 7 summarizes inspections on this blended feed. This operation was carried out in Run 184-194 at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.00 Vo/Hr/Vr corresponding to a catalyst space velocity of 0.107 Bbl/D/Lb. This run lasted 20 days to catalyst age of 2.2 Bbl/Lb at which time it was voluntarily shut down.

Figure 15 shows the desulfurization rate and catalyst deactivation. The initial sulfur removal rate was 65 percent producing 0.68 weight percent sulfur product oil and the final desulfurization rate was 55 percent producing 0.91 weight percent sulfur product. The vanadium removal rate at the beginning of this run was 21 percent and at the end it was 14 percent producing a product with 240 parts per million vanadium (ppm V) and 49 parts per million nickel (ppm Ni).

4.3.2 Products from Medium Level Demetallization at Conditions A, B, and C

The demetallized products from the medium level, 65-75 percent vanadium removal operations, were blended and designated HRI L-401, 405, 406. Table 7 shows the inspections of these feeds.

Three conditions (A, B, and C) were run.

Condition A desulfurization was conducted in Run 184-195 at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.00 Vo/Hr/Vr corresponding to a catalyst space velocity of 0.107 Bbl/D/Lb. Feed designated L-401 was used in this run which lasted 20 days to a catalyst age of 2.3 Bbl/Lb.

Condition B was run using feed L-405 in unit 184-196 at 760°F, hydrogen pressure 2000 psig, liquid space velocity of 0.53 Vo/Hr/Vr corresponding to a catalyst space velocity of 0.056 Bbl/D/Lb. The run lasted 20 days to a catalyst age of 1.1 Bbl/Lb.

TABLE 6 SUMMARY OF INSPECTIONS ON AMERICAN
CYANAMID 0.02" HIGH ACTIVITY BEADED CATALYST

HRI Identification Number	3104
---------------------------	------

Physical Properties

Surface Area, M ² /g	250
H ₂ O Pore Volume, cc/g	(0.67)
Hg Pore Volume, cc/g	0.62

Screen Analysis, U.S. Sieve No.

+20	1.3
20/30	16.9
30/40	76.2
40/50	5.0
50/70	0.5
70/100	0.1
-100	----

Chemical Analysis, W %

MoO ₃	(15.0)
CoO	(3.0)
Al ₂ O ₃	Bal

() Manufacturers Specifications

TABLE 7 FEED STOCK INSPECTIONS

Feedstock: Demetallized Bachaquero Export Vacuum Residuum

Vanadium Removal, % ⁽¹⁾	45	65	65	65	83
HRI Identification No.	L-400	L-401	L-405	L-406	L-408
Gravity, °API	11.3	13.1	14.4	15.0	17.5
Sulfur, W %	1.98	1.39	1.40	1.25	1.00
RCR, W %		13.3	13.9	13.5	10.7
Nitrogen, ppm	4061	4637	4508	4501	3935
Carbon, W %					
Hydrogen, W %					
Vanadium, ppm	305	191	192	190	100
Nickel, ppm	65	48	50	50	34
Viscosity, SFS @ 210°F	216	58	50	32	
SUS @ 210°F			420	348	199
<u>IBP-650°F</u>					
Volume, %	4.0	7.0	9.0	11.0	13.0
Gravity, °API	33.0	33.8	35.2	35.9	36.1
Sulfur, W %	0.43	0.23	0.14	0.11	0.13
<u>650-975°F</u>					
Volume, %	18.7	20.0	23.3	24.7	23.3
Gravity, °API	18.9	20.3	20.7	21.3	21.8
Sulfur, W %	1.07	0.68	0.75	0.67	0.29
<u>975°F+</u>					
Volume, %	77.3	73.0	67.7	64.3	63.7
Gravity, °API	8.2	10.1	8.9	8.7	10.8
Sulfur, W %	2.19	1.71	1.68	1.75	1.29
RCR, W %	20.4	18.4	19.9	21.5	16.6

(1) Compared to feed into demetallization

FIGURE 15

DESULFURIZATION OF LOW LEVEL (40-45% VANADIUM REMOVAL) DEMETALLIZED BACHAQUERO EXPORT VACUUM RESIDUUM

OVER 0.02" HDS BEADS

RUN NO. 184-194

FEED COMPOSITION
HRI - L-400

Gravity, °API 11.3
Sulfur, W % 1.98
Vanadium, ppm 305
Nickel, ppm 65

OPERATING CONDITIONS

H₂ Pressure, psig 2000
Temperature, °F 760
Liquid Sp. Vel., V/Hr/V 1.00
Cat. Sp. Vel. B/D/Lb 0.107

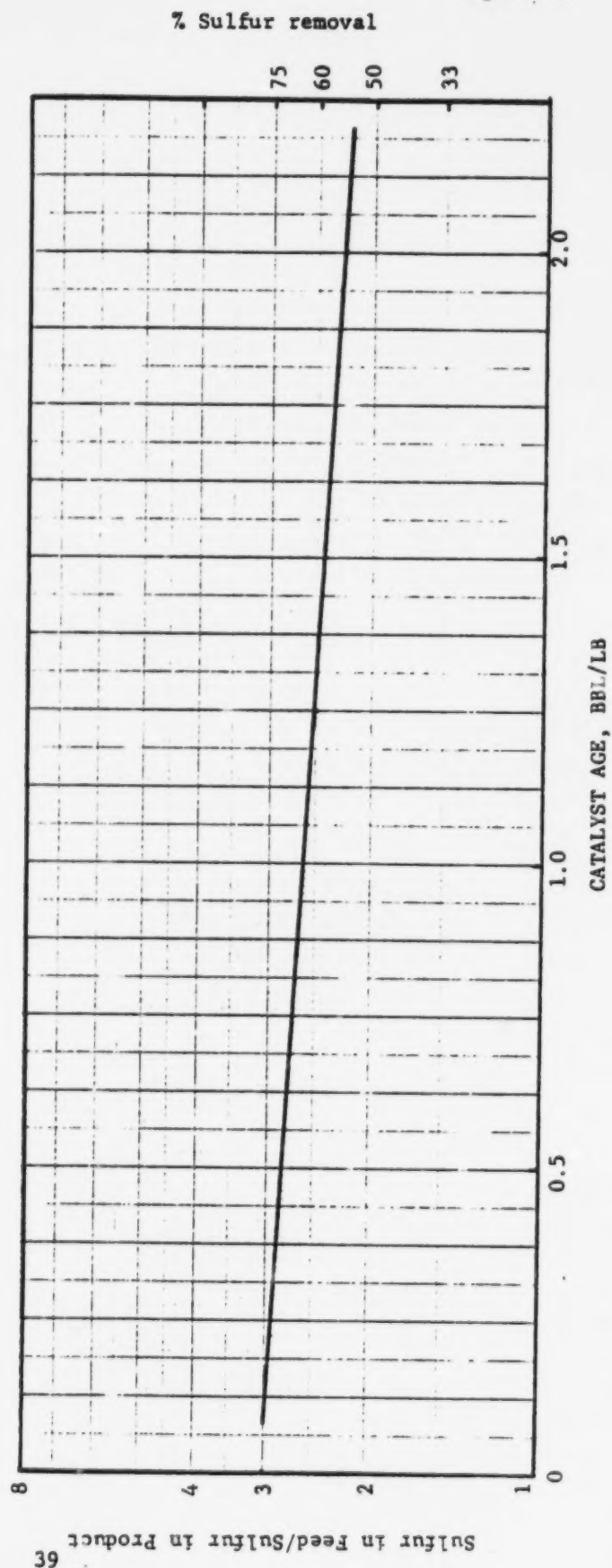


Figure 15

% Sulfur removal

75
60
50
33

2.0

1.5

1.0

0.5

CATALYST AGE, BBL/LB

Sulfur in Feed/Sulfur in Product

Condition C desulfurization was carried out in Run 184-197 using L-405 and 406 feed. The conditions of this operation were 780°F, 2000 psig hydrogen pressure, liquid space velocity of 0.5 Vo/Hr/Vr and catalyst space velocity of 0.052 Bbl/D/Lb.

After six days of operation, hydrogen flow could not be maintained and the run had to be terminated. The hydrogen metering orifice was found to be partially restricted.

A new run was started in unit 185-248 under identical conditions. This run lasted 12 days to catalyst age 0.68 Bbl/Lb before the demetallized feed was exhausted.

The desulfurization results achieved using conditions A, B, and C are plotted in Figure 16. Under condition A, desulfurization achieved was 54 weight percent sulfur removal producing 0.64 weight percent sulfur product containing 159 ppm V and 41 ppm Ni. Under Condition B desulfurization was 72 percent producing 0.4 weight percent sulfur product containing 137 ppm V and 35 ppm Ni, and under condition C 78 percent desulfurization producing 0.3 weight percent sulfur product containing 88 ppm V and 26 ppm Ni.

The rate of catalyst deactivation increases with increasing level of desulfurization. At condition C, the highest level of desulfurization, the catalyst deactivation slope was 0.34 while condition B had a slope of 0.22 and condition A was 0.097.

Figure 17 shows the sulfur level in the products versus catalyst age for conditions A, B, and C.

4.3.3 Products from High Level Demetallization

The demetallized products from the high level demetallization operations, 80-85 percent vanadium removal, were blended and designated as HRI L-408, inspections given in Table 7.

This blend was used as feed to Run 185-249 carried out at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.0 Vo/Hr/Vr corresponding to a catalyst space velocity of 0.107 Bbl/D/Lb. This run lasted 17 days to catalyst age of 1.9 Bbl/Lb using up all the available feedstock. Figure 18 shows the catalyst deactivation with age.

Average desulfurization level achieved during this run was 55 percent sulfur removal producing oil containing 0.45 weight percent sulfur and 66 ppm V and 24 ppm Ni. Figure 19 shows a plot of weight

FIGURE 16

DESULFURIZATION OF MEDIUM LEVEL (65-70% VANADIUM REMOVAL) DEMETALLIZED BACHAQERO EXPORT VACUUM RESIDUUM

OVER 0.02 INCH BEADS

(VANADIUM REMOVED IN DEMETALLIZED STAGE ~ 65%)

DESULFURIZATION FEED CHARACTERISTICS						OPERATING CONDITIONS				
Symbol	Run No.	°API	% S	ppm V	ppm Ni	Condition	Temp °F	PSIG	V/HR/V	B/D/Lb
A	184-195	13.1	1.39	191	48	A	760	2000	1.00	0.107
B	184-196	14.4	1.40	192	50	B	760	2000	0.53	0.056
C	185-248	15.0	1.25	190	47	C	780	2000	0.50	0.052

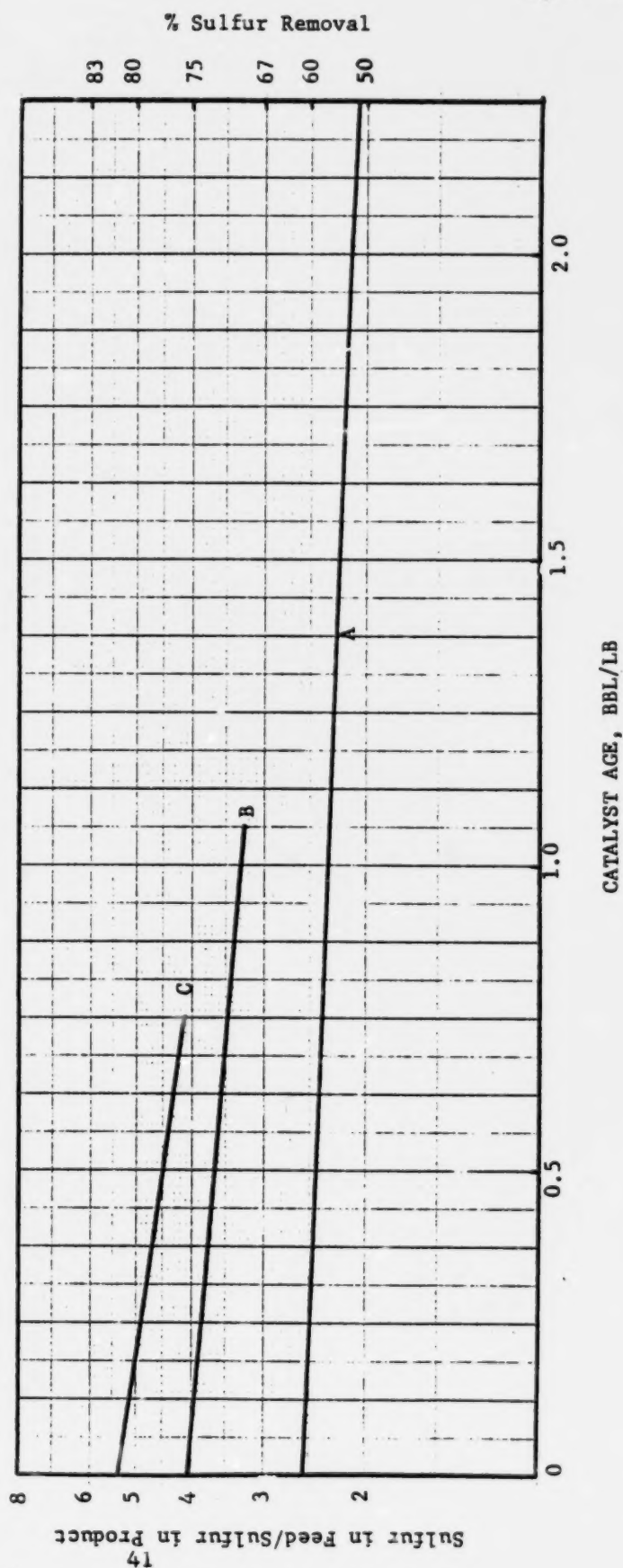


FIGURE 17

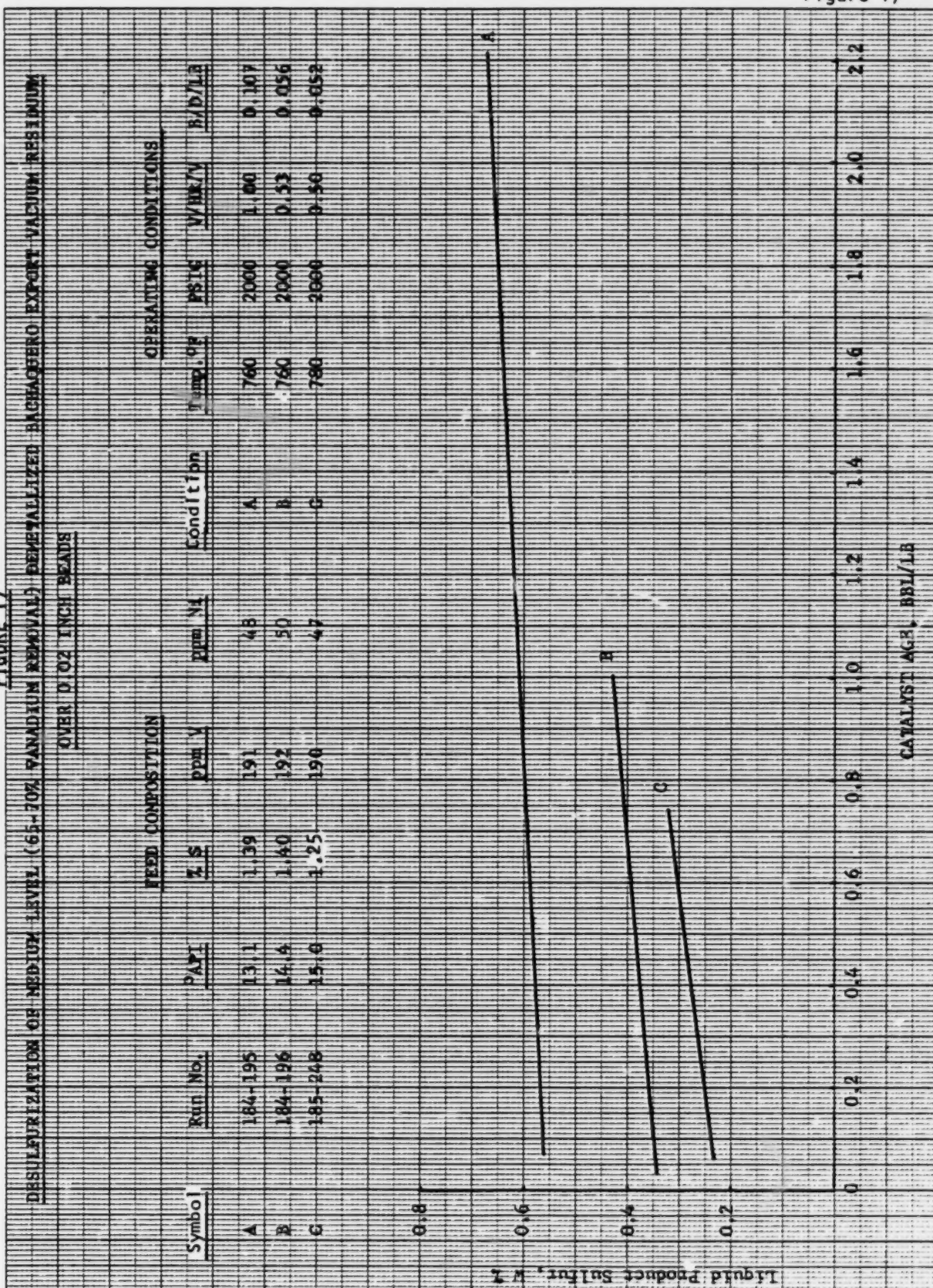


Figure 17

FIGURE 18

DESULFURIZATION OF HIGH LEVEL (80-85% VANADIUM REMOVAL) DEMETALLIZED BACHAQUERO EXPORT VACUUM RESIDUUM

OVER 0.02" BEADS

Run 185-249

FEED COMPOSITION

17.5 °API
1.0 % Sulfur
100 ppm V
34 ppm Ni

OPERATING CONDITIONS

2000 Psig H₂ Pressure
760°F, Reactor Temperature
1.0 V/HR/V Liq. Sp. Vel.
0.107 B/D/LB Cat. Sp. Vel.

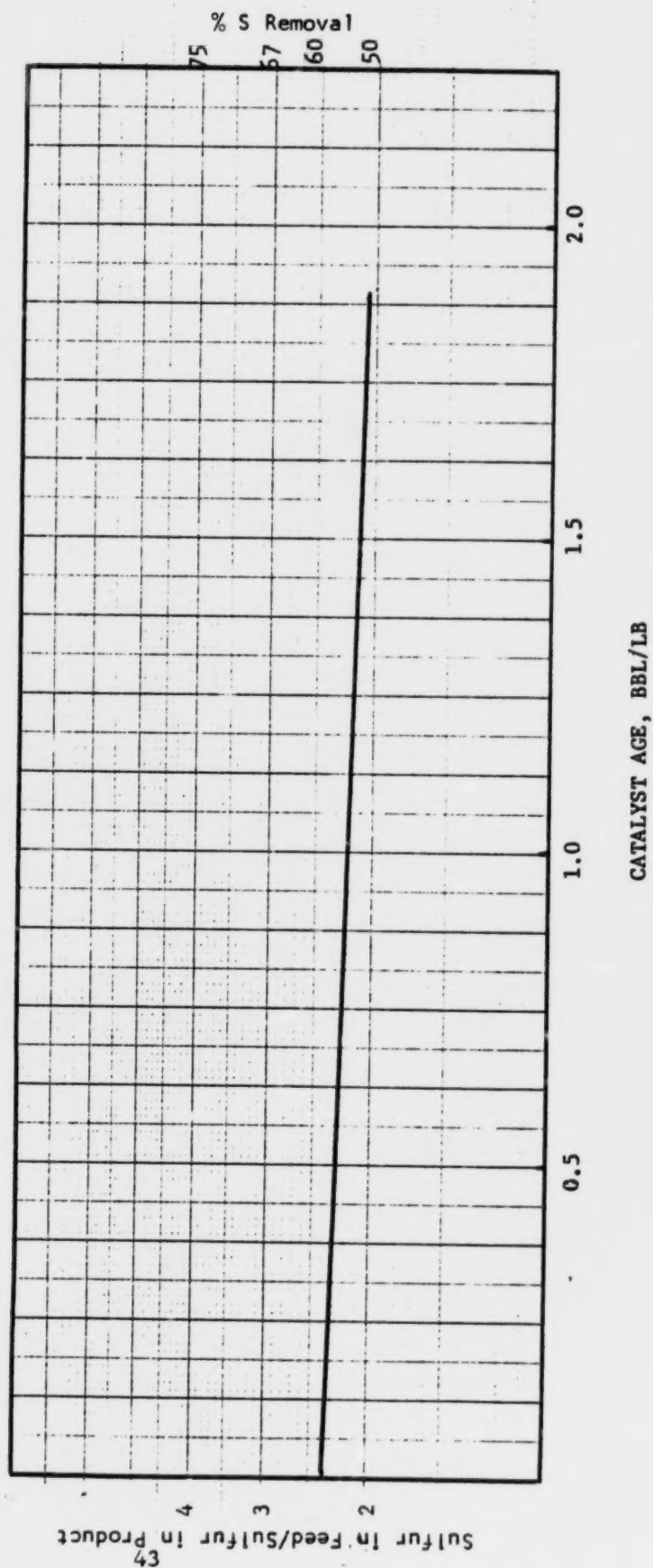


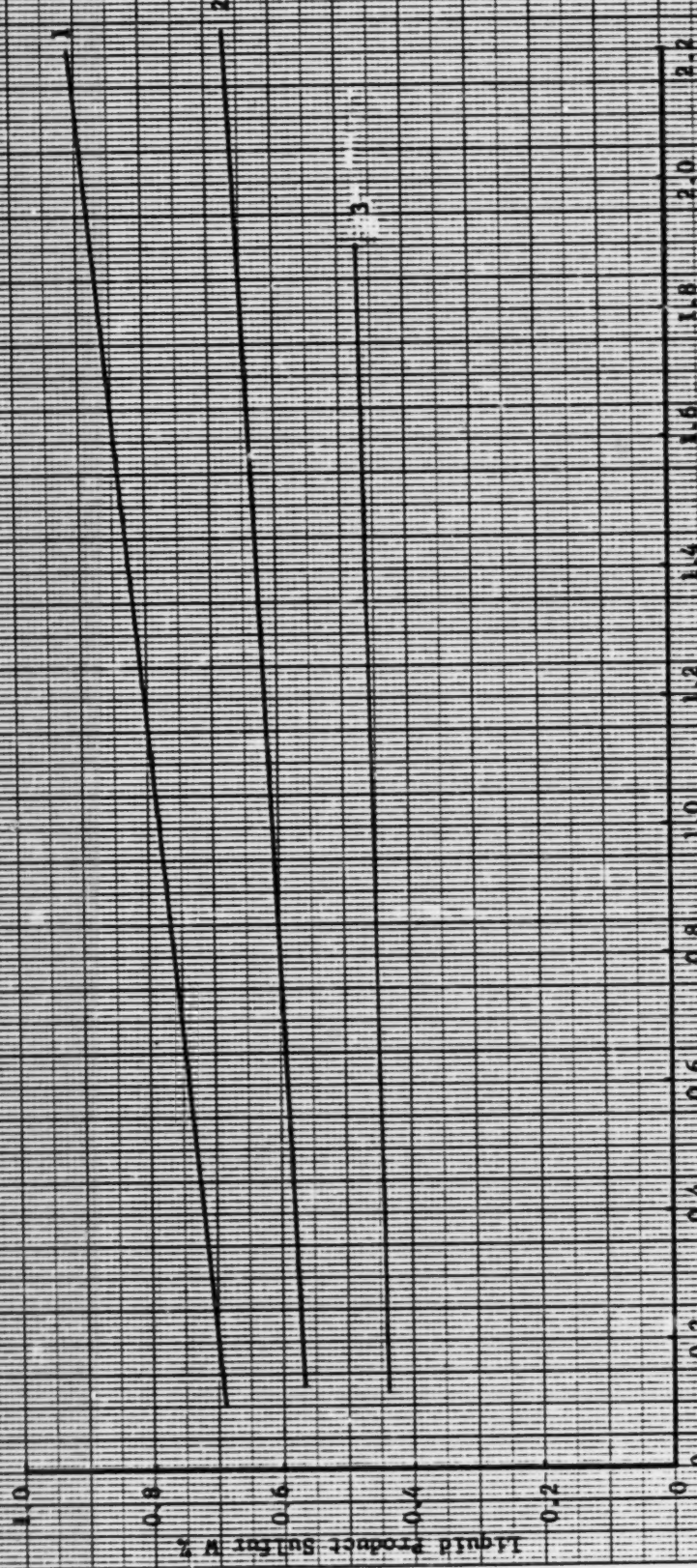
Figure 18

FIGURE 19

DESULFURIZATION OF DEMETALLIZED BACHQUEXCO EXPORT VACUUM RESIDUUM
OVER 0.02" BEADS

LIQUID PRODUCT SULFUR

Symbol	Run No.	FEED COMPOSITION				Z VANADIUM REMOVED IN DEMET. STAGE	H Press PSIG	OPERATING CONDITIONS			Cat. Sp. Vel. B/D/LB.
		API	Wt. %	Wt. %	Wt. %			Temp., °F	Lin. Sp. Vel. W/HR/V		
1	184-194	11.3	1.98	305	65	~ 45 Low level	2000	760	1.0		0.107
2	184-195	13.1	1.39	191	48	~ 65 medium level	2000	760	1.0		0.107
3	185-269	17.5	1.00	100	34	~ 82 High level	2000	760	1.0		0.107



CATALYST AGE, BBL/LB

Figure 19

percent sulfur in the product versus catalyst age and is compared with sulfur levels in the products from low level and medium level demetallization operations conducted at similar desulfurization conditions.

4.4 Demetallized Lloydminster Vacuum Residuum

4.4.1 Products from Medium Level Demetallization

Products from demetallization Run 115-1248 were blended and designated HRI L-422. The inspections on this blended feed are presented in Table 8.

This operation using L-422 as feed was carried out in Run 185-250 at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.0 Vo/Hr/Vr and catalyst space velocity of 0.107 Bbl/D/Lb. This run lasted for 26 days to a catalyst age of 3.0 Bbl/Lb. Aging results from this run are summarized in Figure 20.

4.4.2 Products from High Level Demetallization

Products from demetallization Run 115-1249 were blended and designated HRI L-424, with inspections presented in Table 8.

This operation was carried out in Run 185-251 using L-424 as feed at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.0 Vo/Hr/Vr and catalyst space velocity of 0.107 Bbl/Hr/Lb. This run lasted for 24 days to a catalyst age of 2.9 Bbl/Lb.

Catalyst deactivation with age is plotted in Figure 20, along with results obtained on the lower demetallized feed (45-60% vanadium removal) carried out in Run 185-250. The catalyst slopes of these two runs are about the same, and correlate well with previously determined data on Tia Juana, Bachaquero and Gach Saran which showed that highly demetallized feeds generally give lower deactivation slopes.

Figure 21 shows the sulfur levels versus catalyst age which were achieved during desulfurization of the two levels of demetallized Lloydminster feeds. Sulfur levels ranged from 0.62 to 0.80 weight percent on the lower demetallized feed and from 0.46 to 0.65 weight percent sulfur on the higher demetallized feed. The overall desulfurization was lower on the higher demetallized feed because the last trace of sulfur is more difficult to remove.

TABLE 8 FEED STOCK INSPECTIONS

Feedstock: Demetallized Lloydminster Vacuum Residuum

Vanadium Removed, % ⁽¹⁾	63	85
HRI Identification No.	L-422	L-424
Gravity, °API	13.2	16.4
Sulfur, W %	2.83	1.88
RCR, W %	13.5	9.5
Nitrogen, ppm	4375	3785
Carbon, W %	85.84	85.72
Hydrogen, W %	11.03	11.02
Vanadium, ppm	63	31
Nickel, ppm	59	31
Viscosity, SFS @ 210°F	111	24
SUS @ 210°F	1075	286
<u>IBP-650°F</u>		
Volume, %		12.0
Gravity, °API		34.5
Sulfur, W %		0.41
<u>650-975°F</u>		
Volume, %		27.7
Gravity, °API		20.2
Sulfur, W %		0.89
<u>975°F+</u>		
Volume, %	(65)	60.3
Gravity, °API		9.1
Sulfur, W %		2.21
RCR, W %		16.47

(1) Compared to feed into demetallization

FIGURE 20

DESULFURIZATION OF DEMETALLIZED LLOYDMINSTER VACUUM RESIDUUM

OVER 0.02" BEADS

FEED CHARACTERISTICS

Symbol	Run No.	°API	% S	ppm V	ppm Ni	FEED HRI NO.	% VANADIUM REMOVED In Demet. Stage	OPERATING CONDITIONS		
								psig	Temp. °F	$\frac{V}{Hr/V}$ $\frac{B}{D/Lb.}$
A	185-250	13.2	2.83	63	59	L-422	63	2000	760	1.0 0.107
B	185-251	16.4	1.88	31	31	L-424	82	2000	760	1.0 0.107

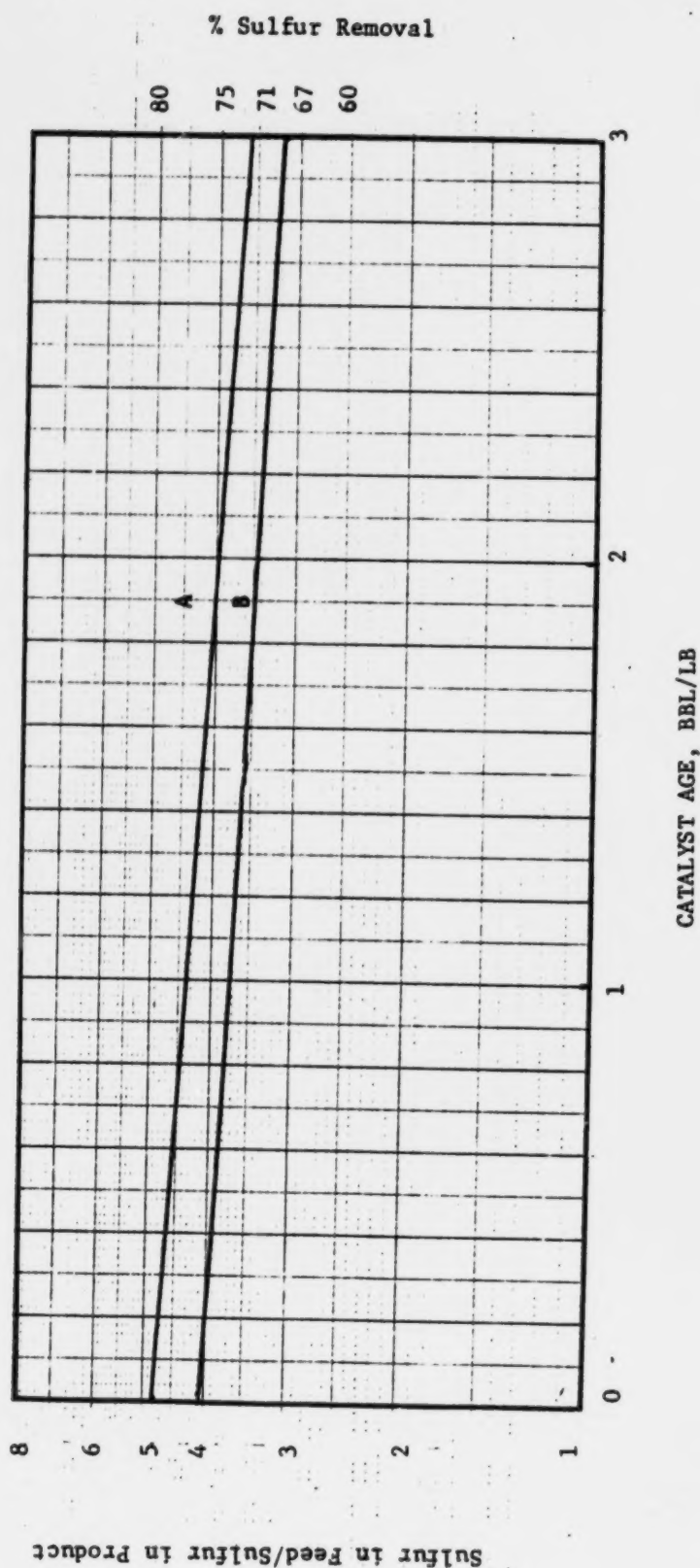


Figure 20

FIGURE 21

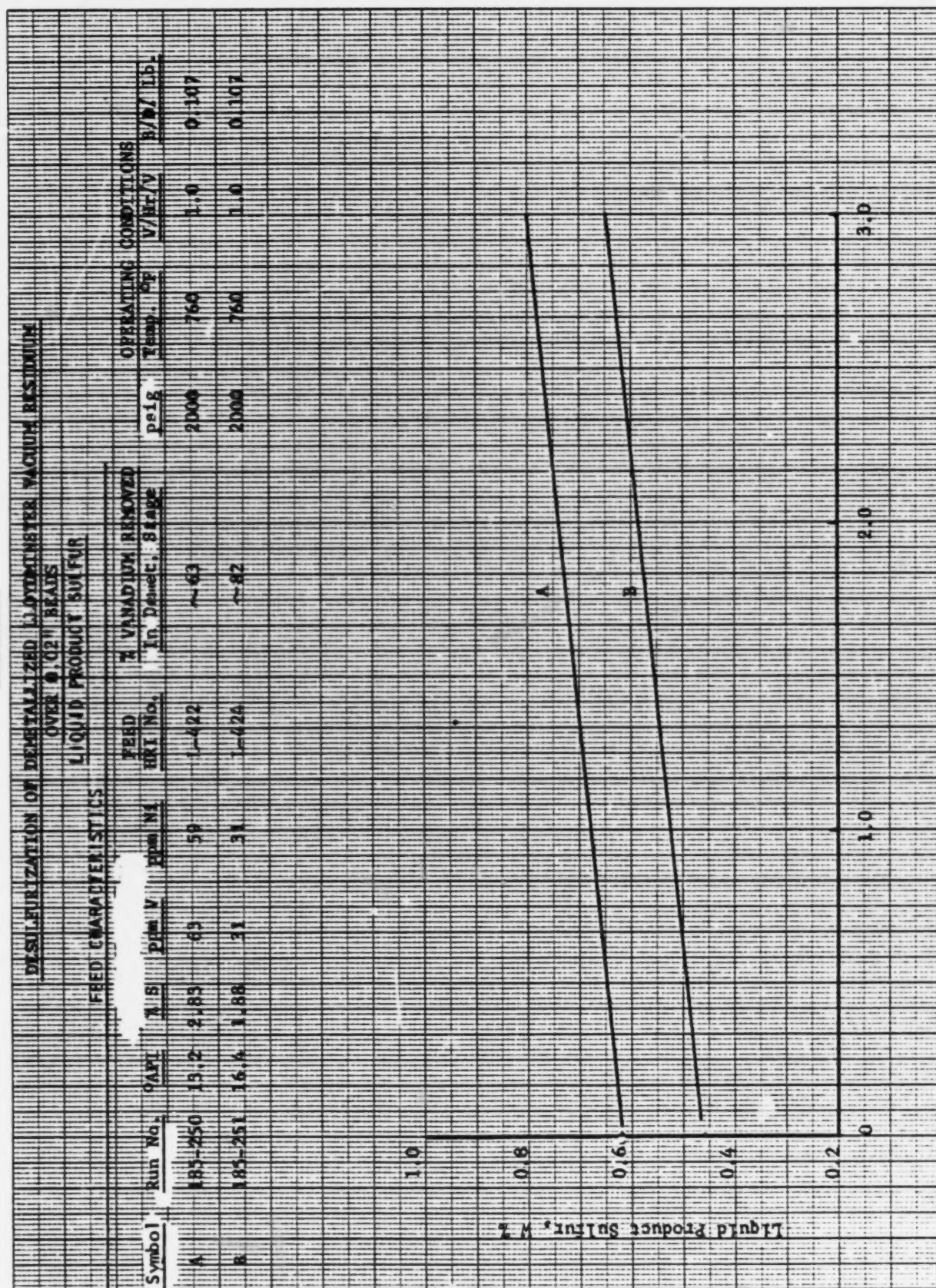


Figure 21

CATALYST AGE, BBL/LB

The amount of vanadium to be removed in the demetallization stage depends on the final sulfur level of the fuel oil. For a given sulfur level fuel oil the optimum combination of vanadium removal in the demetallization stage with optimum sulfur removal in the desulfurization stage is presented below.

Fuel Oil Sulfur Level	% Vanadium Removal in the Demetallization Stage	% Sulfur Removal in the Desulfurization Stage
1 W %	65	60
0.5 W %	75	76.5
0.3 W %	82.5	83.2

4.5 Spent Desulfurization Catalyst Inspections

Analyses on the spent desulfurization catalysts are tabulated in Table 9. The carbon content ranged from about 12 to 20 weight percent but did not correlate with catalyst age, temperature or liquid space velocity.

However, the metals laydown (vanadium & nickel) was strongly influenced by the demetallization level achieved in the demetallization step. For example, feeding Bachaquero Export vacuum residuum which was demetallized to 44 percent metals removal level, deposited 3.65 weight percent metals on the commercial HDS catalyst while the same feed demetallized to 64 percent level deposited only 1.93 weight percent metals on the HDS catalyst at a comparable catalyst age and identical operating conditions.

Similar results were obtained on Lloydminster vacuum residuum. Feed which was demetallized to a 53 percent level, deposited 3.82 weight percent metals on the HDS catalyst while the feed demetallized to a 76 percent level deposited only 1.49 weight percent metals at a comparable catalyst age and operating conditions.

The results on Bachaquero and Lloydminster residua further prove the ability of the newly developed scavenger catalyst to substantially prolong the life of a commercial HDS catalyst as was the case previously demonstrated on Tia Juana and Gach Saran residua.

The pore size distribution of the spent desulfurization catalysts are shown in Table 10. The loss in total pore volumes was not as extensive as was the case with the demetallization catalysts.

TABLE 9 ANALYSES OF SPENT DESULFURIZATION CATALYSTS

RUN NO.		TEMP. °F	LHSV Vo/Hr/Vr	CATALYST AGE Bbl/Lb	WT %			
					C	S	V	Ni
184-194	Bachaquero 40-45% V-Removal	760	1.00	2.20	15.63	6.48	3.07	0.58
184-195	Bachaquero 65-70% V-Removal	760	1.00	2.30	18.44	4.58	1.47	0.46
184-196	Bachaquero 65-70% V-Removal	760	0.53	1.10	14.74	4.90	1.00	0.35
184-197	Bachaquero 65-70% V-Removal	780	0.50	0.45	15.80	2.52	0.52	0.21
184-248	Bachaquero 65-70% V-Removal	780	0.50	0.68	20.51	4.13	0.80	0.28
185-249	Bachaquero 80-85% V-Removal	760	1.00	1.90	20.28	3.68	0.80	0.30
185-250	Lloydminster 45-60% V-Removal	760	1.00	3.00	12.13	6.53	2.22	1.60
185-251	Lloydminster 80-85% V-Removal	760	1.00	2.90	17.73	4.80	0.69	0.80

TABLE 10 PORE SIZE DISTRIBUTION OF SPENT DESULFURIZATION CATALYSTS

SPENT CATALYST From Run No.	CATALYST AGE Bbl/Lb	WT %		PORE DIAMETER RANGE ANGSTROMS				TOTAL PORE VOLUME cc/g	LOSS IN TOTAL PORE VOLUME %
		C	V + Ni	30-50	50-70 PORE VOLUME	70-100	100+		
Fresh 3401	---	---	---	0.114	0.207	0.161	0.087	0.569	---
184-194	2.20	15.63	3.65	0.128	0.129	0.047	0.049	0.353	38.0
184-195	2.30	18.44	1.93	0.124	0.085	0.043	0.045	0.297	47.8
184-196	1.10	14.74	1.35	0.100	0.170	0.072	0.070	0.412	27.6
184-197	0.45	15.80	0.73	0.105	0.150	0.070	0.067	0.392	31.1
185-248	0.68	20.51	1.08	0.114	0.095	0.043	0.055	0.307	46.0
185-249	1.90	20.28	1.10	0.148	0.051	0.021	0.030	0.250	56.1
185-250	3.00	12.13	3.82	0.084	0.151	0.104	0.049	0.388	31.8
185-251	2.90	17.73	1.49	0.112	0.109	0.055	0.057	0.333	41.5

Note: Pore size distribution and total pore volumes on spent catalysts were corrected to fresh catalyst basis. (See section 4.6 for method used.)

4.6 Desulfurization Correlations

The effect of residual metals (vanadium & nickel) in the demetallized feed on the deactivation slope of the commercial HDS catalyst is shown in Figure 22. Depicted are results obtained on Bachaquero Export and Lloydminster vacuum residua from the present Phase III work and data obtained on Tia Juana and Gach Saran vacuum residua under Phase II work.

Results from data accumulated on Bachaquero Export vacuum residuum indicated that the higher the level of metals removal in the demetallization stage, the lower would be the deactivation slope of the commercial HDS catalyst. However, above 65 percent vanadium removal, corresponding to about 240 ppm metals, the increase in the deactivation slope is only about one half of that between 45 and 65 percent vanadium removal.

For Lloydminster vacuum residuum the difference in the deactivation slopes between 63 and 82 percent vanadium removal was quite small, less than 0.1. Figure 23 summarizes the contaminant metals deposited on the desulfurization catalyst versus metals in the demetallized feed with each feed at approximately the same catalyst age. As expected, less metals are deposited on the catalyst feeding lower metals containing feed, with a corresponding increased life expectancy of the desulfurization catalyst.

The most important factor to influence deactivation of the desulfurization catalyst appears to be the level of the desulfurization operation being carried out. Figure 24 shows the variation in the deactivation slope versus desulfurization level on Bachaquero Export demetallized to 65 percent vanadium removal level. Variation in the desulfurization level was achieved by varying the liquid space velocity between 0.5 and 1.0 $\text{Vo}/\text{Hr}/\text{Vr}$ and varying the temperature between 760 and 780°F. The catalyst deactivation slope increases by a factor of three for an increase in the desulfurization level from 60 percent to 80 percent. This sharp increase in the rate of catalyst deactivation as indicated in Figure 24 seems to suggest that the rate of sulfur removal for Bachaquero Export feed is strongly diffusion controlled as was the case with vanadium removal in the demetallization step (See section 3.7 for explanation). A demetallization catalyst with the added ability to remove sulfur during demetallization would be an ideal catalyst to produce low sulfur fuel oil in a two stage demetallization process. This is so because the level of sulfur removal that is necessary in the second step to achieve a low sulfur fuel oil would be greatly decreased thus allowing HDS in the regime of slow catalyst deactivation. The newly developed demetallization catalyst appears to fit the above requirements.

FIGURE 22

EFFECT OF METALS CONTENT OF DEMETALLIZED FEEDS

DEACTIVATION SLOPE OF THE DEMETALLIZATION CATALYST

Symbol Feed Identification

- Libby-Inster Vacuum Residue
- Bache and Export Vacuum Residue
- Gach Saran Vacuum Residue
- △ Tia Maria Vacuum Residue

Slope of a plot of $\ln \frac{S_0}{S}$ vs catalyst age

H₂ Pressure 2000 psig

Temperature 760 °F

LHSV 1.0 V/M-FV

Catalyst 0.024 MDS Beads

VANADIUM + NICKEL
IN
DEMETALLIZED FEED, PPM

Slope of deactivation slope

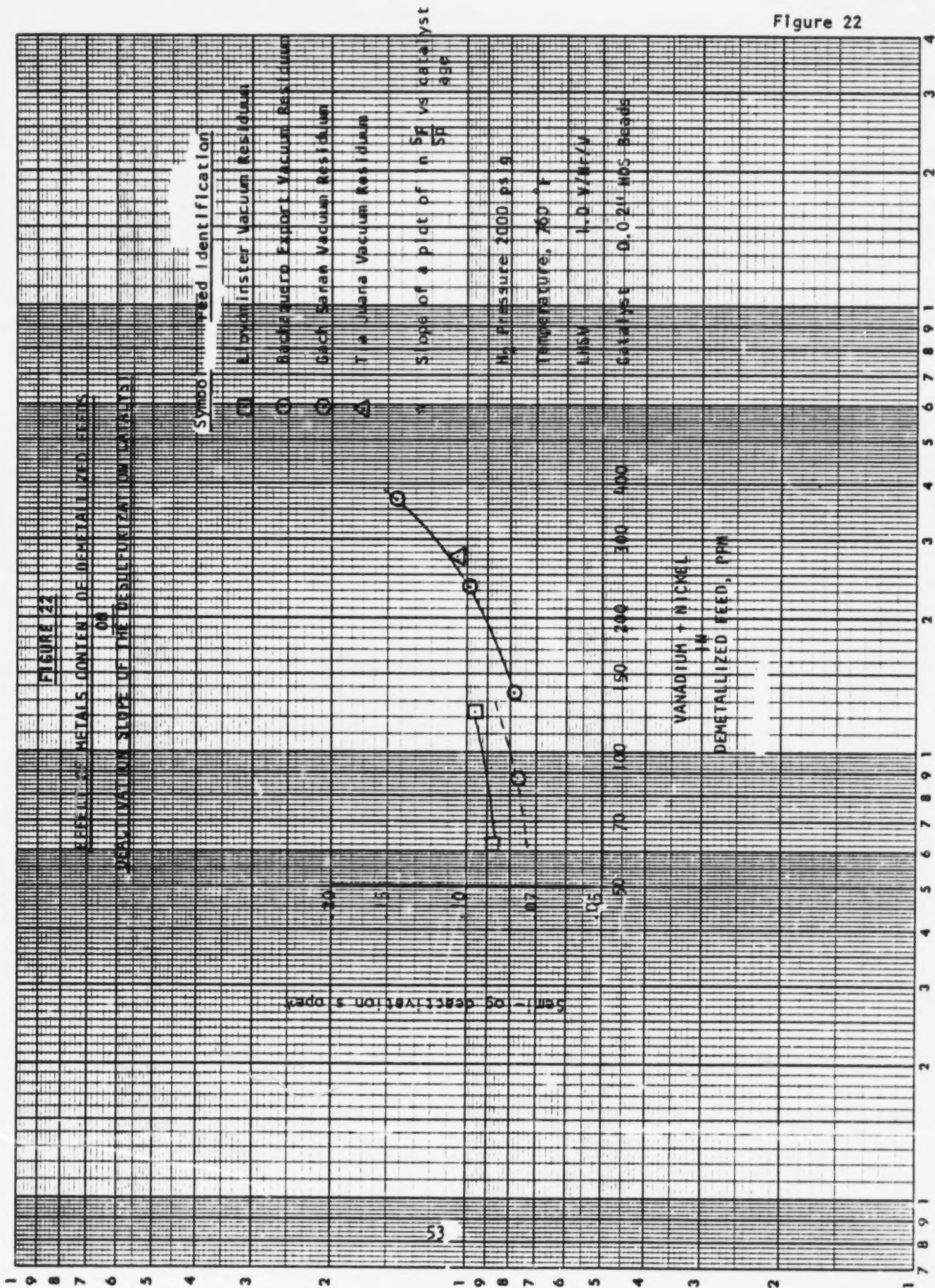


Figure 22

FIGURE 23

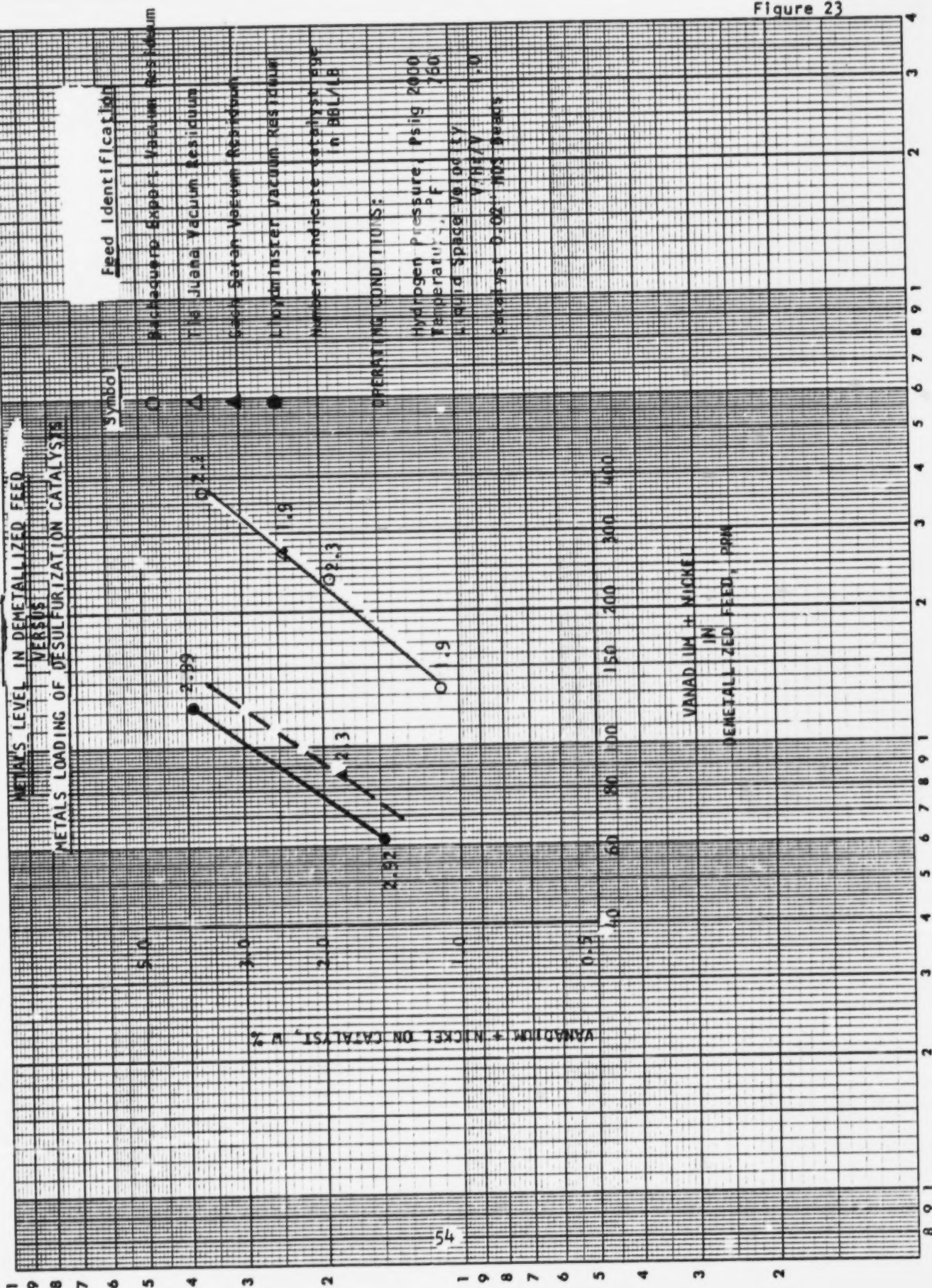


Figure 23

Figure 24

EFFECT OF LEVEL OF DESULFURIZATION ON DEACTIVATION SLOPE OF DESULFURIZATION CATALYSTS

Feed: Demetallized Bachaquero Export Vacuum Residuum
(191 PPM V, 48 PPM Ni)

Operating Conditions:

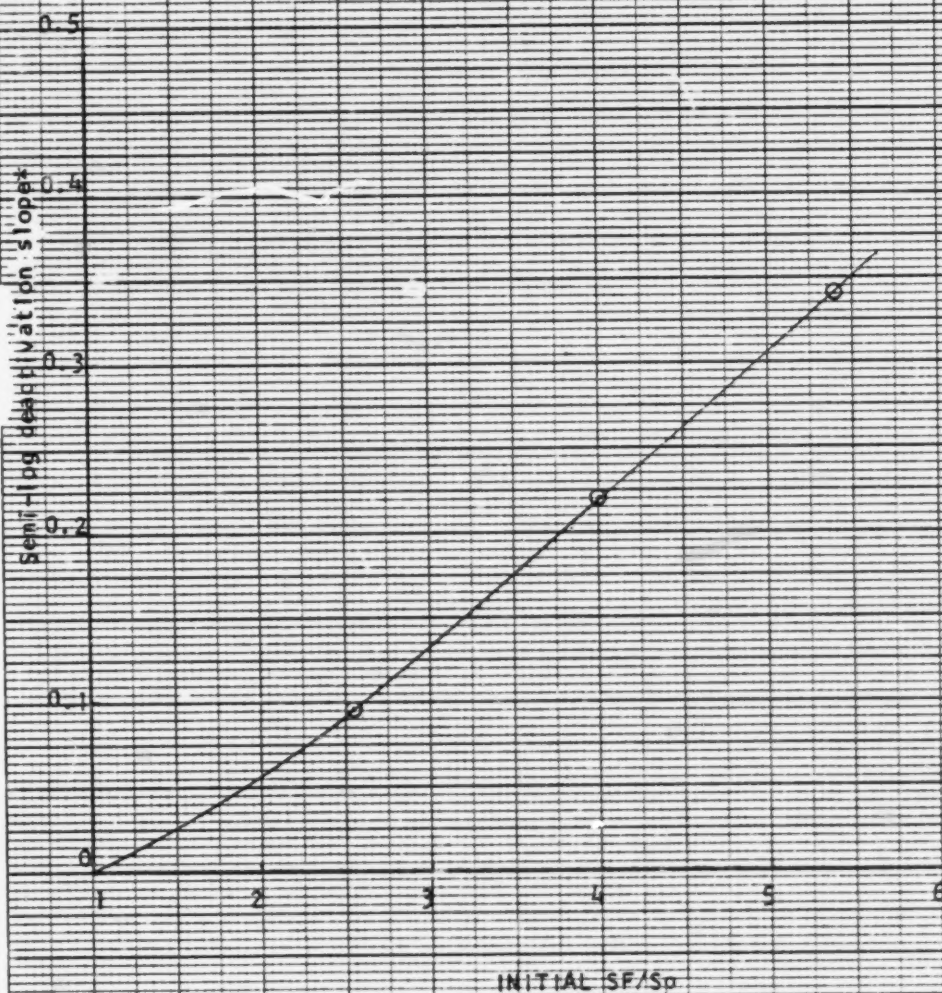
H₂ Pressure, Psig 2000

Temperature, °F 760-780

Liquid Space Velocity, V/Hr/V 0.5 to 1.0

Catalyst 0.02" HDS Beads

* Slope of a plot of $\ln \frac{SF}{Sp}$ vs catalyst age



4.7 Correlated Fuel Oil Properties

Detailed inspections were obtained on products from each desulfurization run. Two twenty-four hour periods were analyzed, one near the beginning of the run and the other near the end of the run. Summaries of product yields and inspections are given in Tables B-1 to B-13 of the Appendix B.

Viscosity variation as a function of API gravity for fuel oils obtained from Bachaquero Export and Lloydminster vacuum residua are presented in Figure 25. Variation of pour point with viscosity on the 400°F+ fuel oils is given in Figure 26, and for the 650°F+ fuel oils in Figure 27.

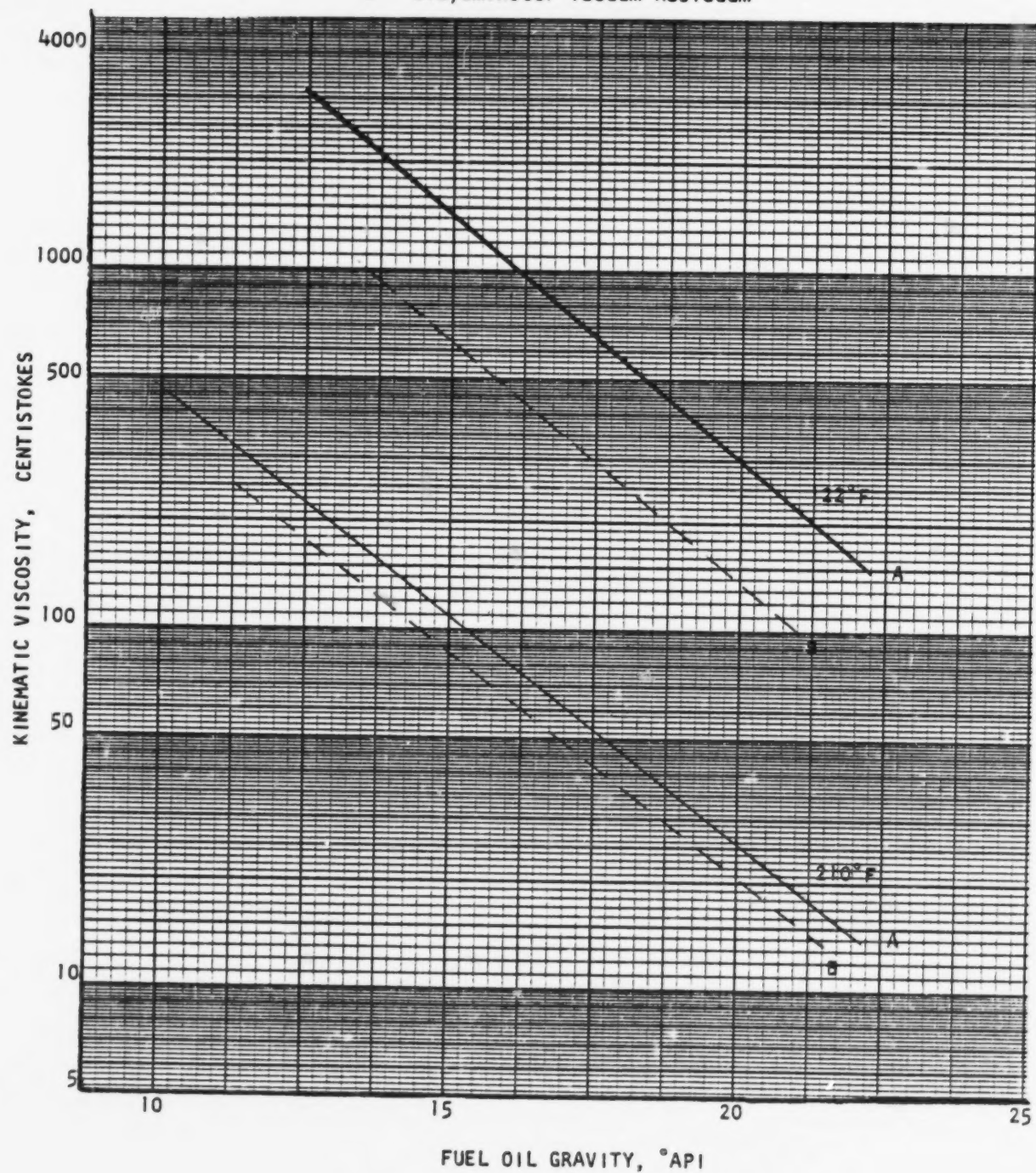
Viscosity determinations were performed using ASTM D-88 "Standard Method of Test for Saybolt Viscosity" at standard temperatures of 122 and 210°F.

The pour point determinations were performed using ASTM D-97 "Standard Method of Test for Pour Point of Petroleum Oils."

Figure 25

FUEL OIL VISCOSITY VS. °API GRAVITY

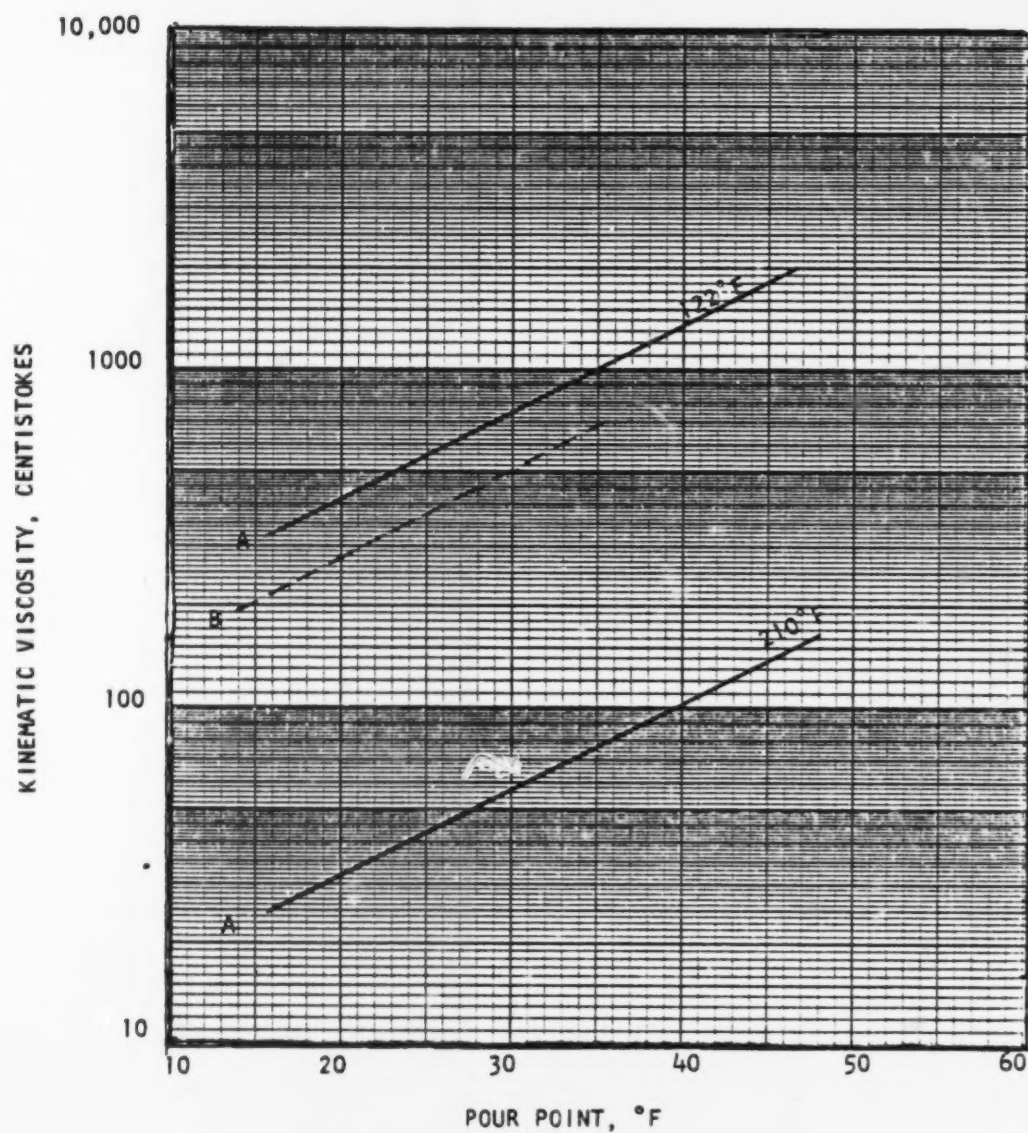
- A Bachaquero Export Vacuum Residuum
- B Lloydminster Vacuum Residuum



400°F+ FUEL OIL VISCOSITY VS. POUR POINT

A Bachaquero Export Vacuum Residuum

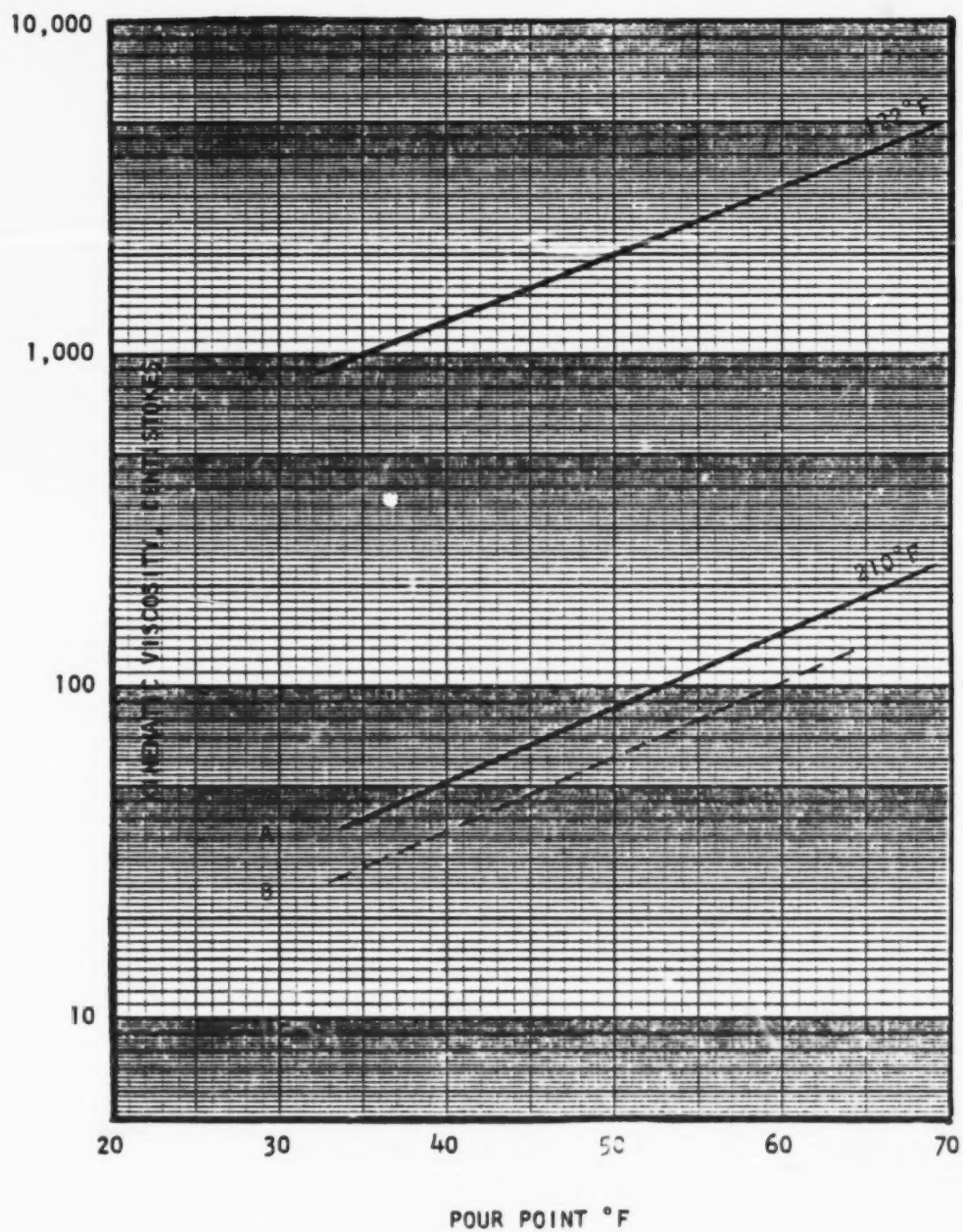
B Lloydminster Vacuum Residuum



650°F+ FUEL OIL VISCOSITY VS. POUR POINT

A Bachaquero Export Vacuum Residuum

B Lloydminster Vacuum Residuum



5. PROCESS ECONOMICS

The major costs in producing low sulfur fuel oil from vacuum residua depend on the cost of the facility necessary to carry out the demetallization and desulfurization operations, the amount of hydrogen consumed during the process, and the cost of the demetallization and desulfurization catalysts. Summaries have been prepared of the processing costs, including investment requirements for producing 1.0, 0.5 and 0.3 weight percent sulfur fuel oil from Bachaquero Export and Lloydminster vacuum residua utilizing the commercially prepared 1.0 weight percent molybdenum on 20 x 50 mesh activated bauxite in the demetallization step and commercial HDS beads in the desulfurization step. These results are given in Tables 11 and 12.

Data used in cost computations for the Bachaquero Export vacuum residuum cases and the 0.5 and 1.0 weight percent sulfur fuel oil cases for the Lloydminster residuum required only a small amount of extrapolation from the operating conditions used in the experimental program. For the 0.3 weight percent sulfur fuel oil case from the Lloydminster feed, a greater extrapolation of the data was necessary.

Curves showing the variation of the overall operating cost for producing 1.0, 0.5, and 0.3 weight percent sulfur fuel oil as a function of vanadium removal in the demetallization stage for the Bachaquero and Lloydminster feeds are given in the Exhibit A portion of Figures 28 and 29. These operating costs include capital charges of 25 percent on investment. The cost calculations are based on 1976 Gulf Coast construction costs and are for a 20,000 barrels per day plant, which is perhaps the minimum size plant that a refiner would build. These operating costs would be lowered as the plant capacity is increased.

Figure 28, Exhibit A shows that for Bachaquero Export vacuum residuum, there were optimum demetallization levels which minimize overall operating costs for the production of 1.0 and 0.5 percent sulfur fuel oil. The 0.5 weight percent sulfur fuel oil curve shows the optimum demetallization to be about 55 percent vanadium removal, corresponding to a total operating cost of \$2.72 per barrel. The optimum demetallization for producing 1.0 weight percent sulfur fuel oil appears to be about 45 percent vanadium removal, the condition utilized in the experimental program. At this optimum level, the total operating cost is \$2.01 per barrel. Costs for producing 0.3 weight percent sulfur fuel oil decreased with increasing levels of demetallization, but it was difficult to achieve sustained vanadium

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TABLE 11
INVESTMENT AND OPERATING COST FOR A TWO STAGE
DEMETALLIZATION - DESULFURIZATION
OPERATION OF BACHAQUERO EXPORT
VACUUM RESIDUUM

<u>BASES</u>		1. Plant Capacity - 20,000 BPSD	2. 1976 Gulf Coast Construction
	3. Hydrogen Cost - \$1.0/MSCF	4. Power - \$0.025/KWH	
	5. Fuel - \$2.0/MMBTU	6. Steam - \$2.5/1000 Lb.	
	7. Process Water - \$0.25/1000 Gal.	8. Cooling Water - \$0.04/1000 Gal.	
	9. Demetallization Catalyst - \$0.35/Lb.	10. Desulfurization Catalyst - \$2.0/Lb.	
	11. Capital Charges - 25% of investment included in the operating cost.		
% Vanadium removed in Demetallization Stage		45	65
			80
<u>1 W % Sulfur Fuel Oil</u>			
	Investment, MM\$	15.93	18.89
	Operating Cost, \$/BBL	2.017	2.155
<u>0.5 W % Sulfur Fuel Oil</u>			
	Investment, MM\$	20.58	23.80
	Operating Cost, \$/BBL	2.763	2.740
<u>0.3 W % Sulfur Fuel Oil</u>			
	Investment, MM\$	24.12	28.13
	Operating Cost, \$/BBL	4.323	3.737
			35.22
			3.528

TABLE 12

INVESTMENT AND OPERATING COST FOR A TWO STAGE
DEMETALLIZATION - DESULFURIZATION
OPERATION OF LLOYDMINSTER
VACUUM RESIDUUM

<u>BASES</u>	1. Plant Capacity - 20,000 BPSD	2. 1976 Gulf Coast Construction	
	3. Hydrogen cost - \$1.0/MSCF	4. Power - \$0.025/KWH	
	5. Fuel - \$2.0/MMBTU	6. Steam - \$2.5/1000 Lb.	
	7. Process Water - \$0.25/1000 Gal.	8. Cooling Water - \$0.04/1000 Gal.	
	9. Demetallization Catalyst - \$0.35/Lb	10. Desulfurization Catalyst - \$2.0/Lb	
	11. Capital Charges - 25% of investment included in the operating cost.		
% Vanadium removed in Demetallization Stage	65	80	85
<u>1 W % Sulfur Fuel Oil</u>			
Investment, MM\$	16.24	18.50	19.90
Operating Cost, \$/BBL	2.122	2.199	2.257
<u>0.5 W % Sulfur Fuel Oil</u>			
Investment, MM\$	19.73	22.37	23.80
Operating Cost, \$/BBL	2.678	2.650	2.672
<u>0.3 W % Sulfur Fuel Oil</u>			
Investment, MM\$	23.98	27.32	29.78
Operating Cost, \$/BBL	3.196	3.082	3.082

461510

Figure 28
TOTAL OPERATING COST FOR A

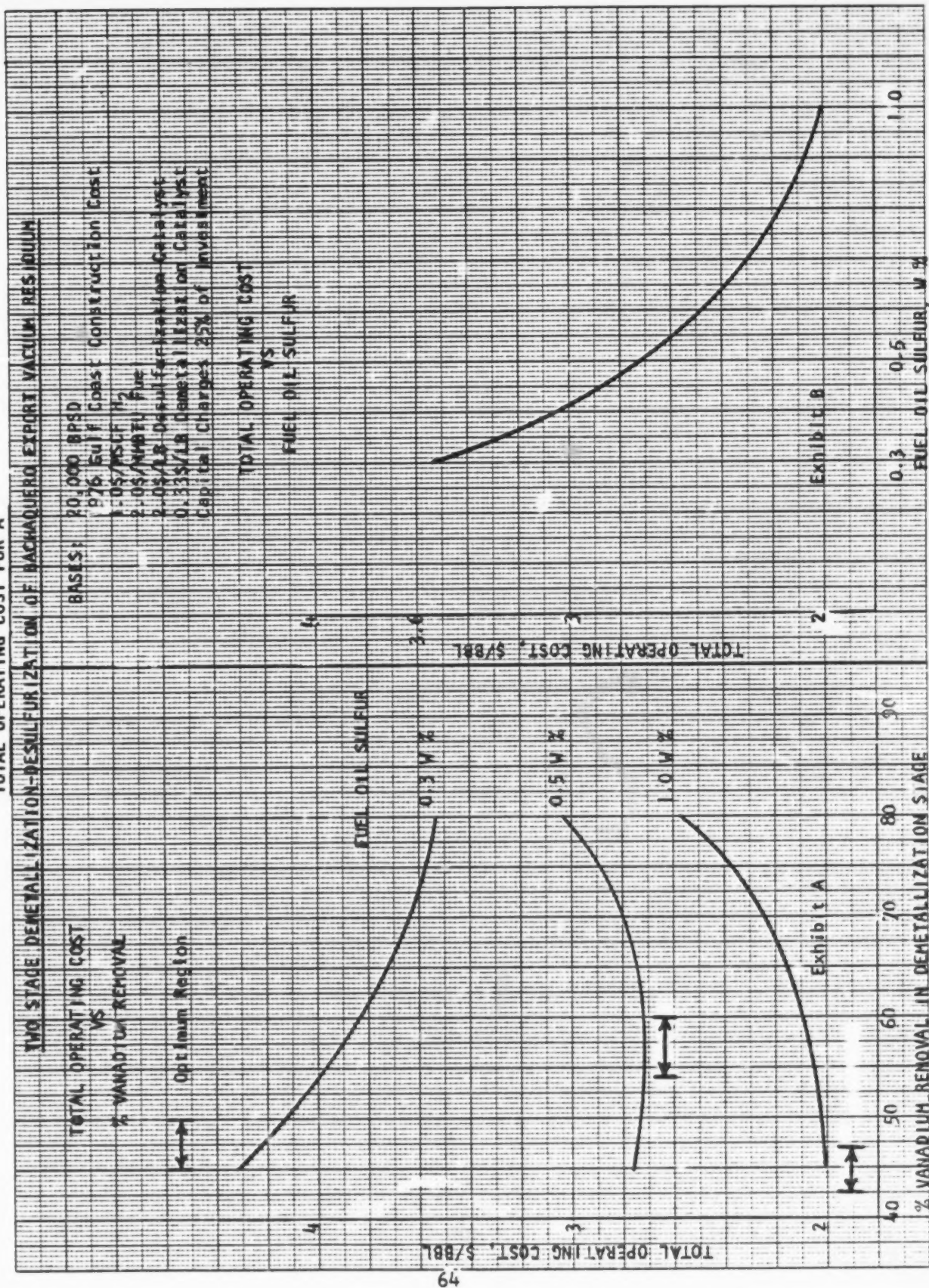


Figure 28

removal above 80 percent, due to the rapid rate of catalyst deactivation. However, the actual removal of metals beyond this level is believed to be of limited economic value since these metal compounds are hard to remove in the demetallization step and, therefore, are also not easily deposited on the desulfurization catalyst.

The variation in total operating cost as a function of fuel oil sulfur level for the Bachaquero feed is summarized in the form of a plot in Figure 28, Exhibit B. These results show that an additional cost of 71 cents per barrel was required to go from 1 to 0.5 weight percent sulfur and an additional 82¢/Bbl was required to go from 0.5 to 0.3 weight percent sulfur.

The saving in overall operating cost by the inclusion of the demetallization step in the process for the Bachaquero feed is summarized in Figure 30. The savings ranged from 44¢/Bbl for the one weight percent sulfur fuel oil to \$1.15/Bbl for the 0.3 weight percent sulfur fuel oil.

Figure 29, Exhibit A shows that for Lloydminster vacuum residuum feed (lower metals, high sulfur feed), there were also optimum demetallization levels which minimize overall costs for the production of fuel oils. The one weight percent fuel oil curve shows the optimum demetallization to be about 65 percent vanadium removal which corresponds to a total operating cost of \$2.12 per barrel. The optimum demetallization for producing 0.5 weight percent sulfur fuel oil is about 75 percent vanadium removal and corresponds to a total operating cost of \$2.64 per barrel. The optimum demetallization for producing 0.3 weight percent sulfur fuel oil is about 83 percent vanadium removal. The overall operating cost for this operation is \$3.08 per barrel.

Figure 29, Exhibit B summarized the variation in overall operating cost as a function of fuel oil sulfur levels for the Lloydminster feed. These results indicate that the incremental cost to produce 0.5 weight percent sulfur fuel oil is 52¢/Bbl over the cost to produce one weight percent sulfur fuel oil. Another incremental cost of 44¢/Bbl, over the cost of producing 0.5 weight percent sulfur fuel oil, is necessary for the production of 0.3 weight percent fuel oil.

No direct desulfurization data on Lloydminster vacuum residuum was available to make a cost comparison against a two stage demetallization/desulfurization operation.

Estimated yield structure and product properties for the

Figure 29

TOTAL OPERATING COST FOR A

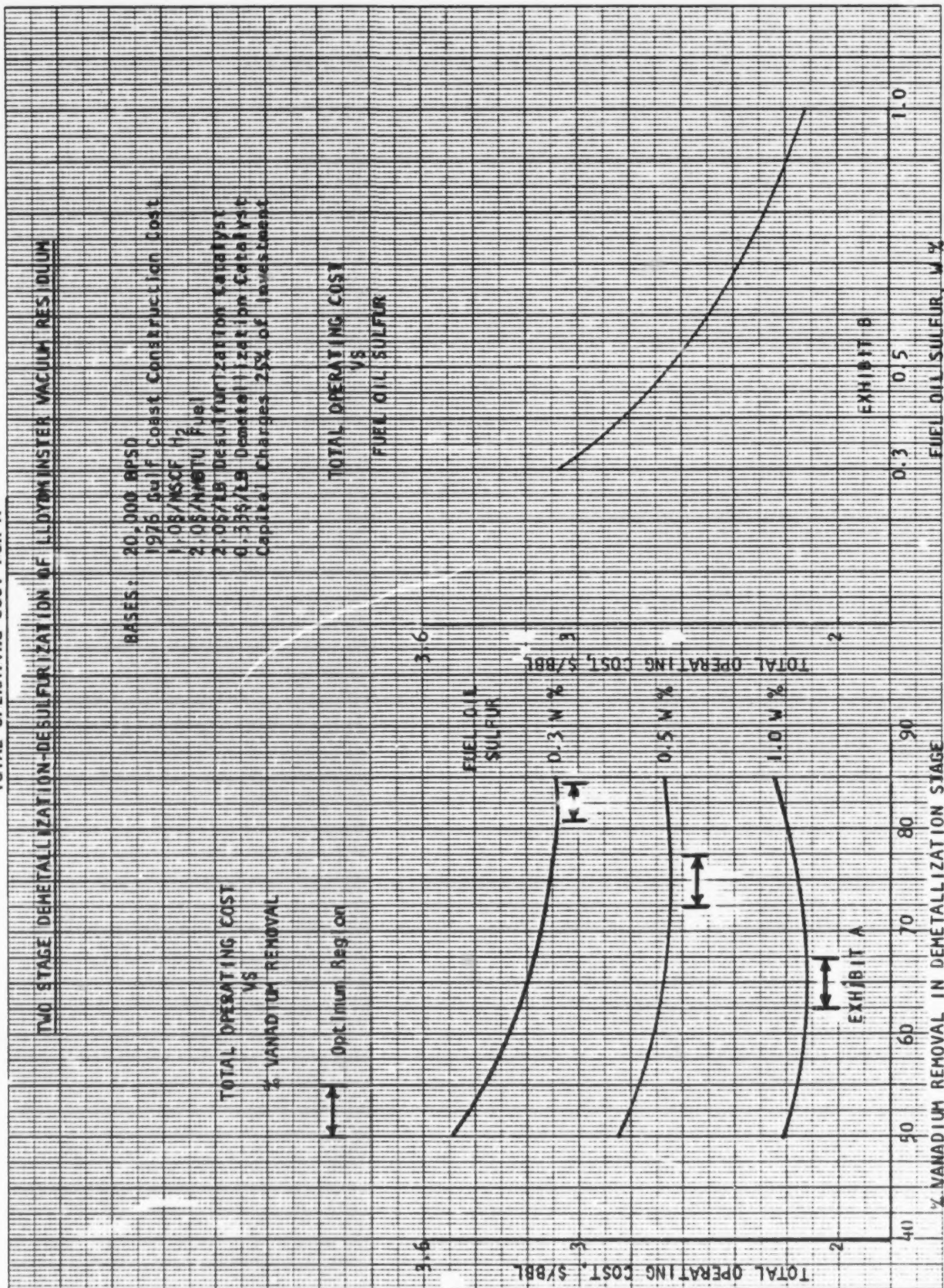
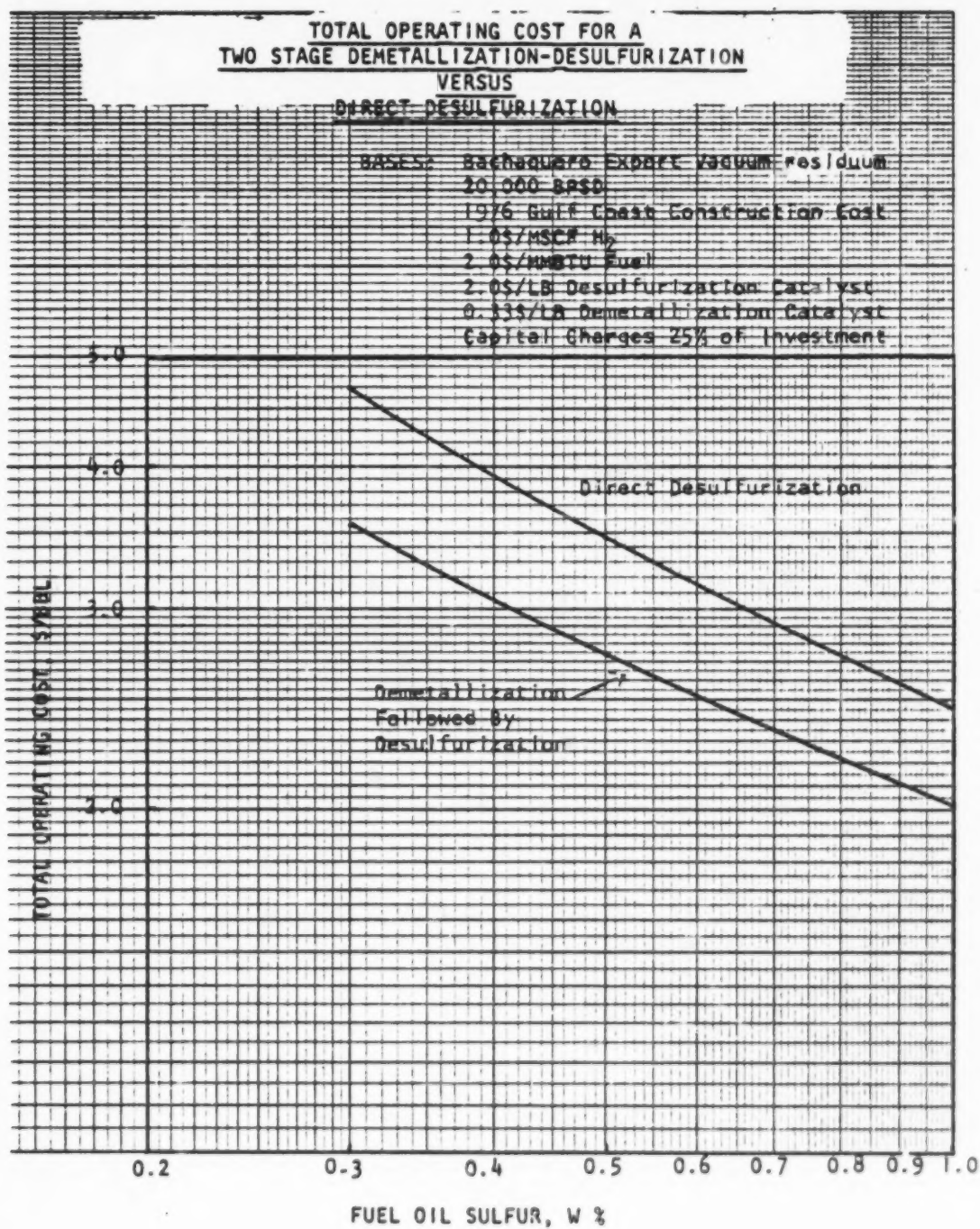


Figure 29

Figure 30



production of 400°F+ fuel oil containing 1.0, 0.5 and 0.3 weight percent sulfur from Bachaquero Export and Lloydminster vacuum residua are given in Table 13 and 14 respectively.

Table 13 ESTIMATED OVERALL YIELDS AND PRODUCT PROPERTIES FROM
CONSECUTIVE DEMETALLIZATION AND DESULFURIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM

400°F+ Fuel Oil Sulfur, W %	1.0	0.5	0.3
<u>Yields</u>			
H ₂ S & NH ₃			
	W% 2.4	W% 3.0	W% 3.3
	%S	%S	%S
C ₁ -C ₃			
	W% 0.8	W% 1.5	W% 1.7
	%S	%S	%S
C ₄ -400°F			
	W% 1.5	W% 3.6	W% 5.1
	%S <0.03	%S <0.03	%S <0.03
400-650°F			
	W% 6.8	W% 10.6	W% 12.4
	%S 0.07	%S 12.6	%S 14.7
650-975°F			
	W% 23.9	W% 30.0	W% 32.0
	%S 26.4	%S 33.4	%S 35.5
975°F+			
	W% 65.6	W% 52.8	W% 47.1
	%S 11.5	%S 54.5	%S 12.5
400°F+			
	W% 96.3	W% 93.4	W% 91.5
	%S 101.8	%S 100.5	%S 99
TOTAL			
	W% 101.0	W% 101.5	W% 101.6
	%S 103.8	%S 105.5	%S 106.0
	°API 16.2	°API 19.7	°API 21.2
	%S 0.97	%S 0.47	%S 0.28

Table 14 ESTIMATED OVERALL YIELDS AND PRODUCT PROPERTIES FROM

CONSECUTIVE DEMETALLIZATION AND DESULFURIZATION OF LLOYDMINSTER VACUUM RESIDUUM

	400°F+ Fuel Oil Sulfur, W %	1.0	-----	0.5	-----	0.3	-----		
<u>Yields</u>		<u>W%</u>	<u>V%</u>	<u>°API</u>	<u>%S</u>	<u>W%</u>	<u>V%</u>	<u>°API</u>	<u>%S</u>
H ₂ S & NH ₃		5.1				5.7			
C ₁ -C ₃		1.1				1.6			
C ₄ -400		1.7	2.2	55	<0.03	2.2	3.0	55	<0.03
400-650°F		8.0	9.4	30	<0.03	11.3	13.3	30	<0.03
650-975°F		34.4	38.0	21	0.28	39.3	43.5	21	0.19
975°F+		51.0	52.7	11	1.64	41.5	43.2	12	0.92
400°F+		93.4	100.1	16.3	1.0	92.1	100.0	18.2	0.5
TOTAL		101.3	102.3	16.9	0.98	101.6	103.0	19.2	0.49
						101.7	103.7	21.0	0.29

APPENDICES

Table A SUMMARY OF DETAILIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Catalyst Promoter	Preparation	Feed	Temp. °F	H ₂ Pres. psia	Space Velocity V/Hr/Wr B/D/Lb	H ₂ Rate SCF/bbl	Cat. Age, Bbl/Lb	Product Inspections				18P- 550°F V %
											Gravity °API	% S	V ppm	NI ppm	
115-1233-1C 2A 2B 3A 3B 4A 4B 5A 5B 6A	3634	Porocel 20 x 50 Mesh	1% Mo	Engelhard Commercial	Bachaquero Export Vacuum Residuum L-397	789	2030	1.47	4300	.136	12.8	2.09	310	65	3
						791	2020	1.44	4580	.190					
						791	2020	1.52	4580	.248	12.7	2.01	311	67	1
						789	1990	1.54	3920	.307					
						789	1990	1.51	3920	.364	12.5	2.01	315	65	1
						790	2000	1.50	4370	.421					
						790	2000	1.48	4370	.477	12.1	2.00	310	63	6
						790	2000	1.49	3950	.534					
						790	2000	1.46	3950	.589	11.6	2.02	308	63	7
						792	1950	1.32	3650	.639	12.0	1.97	307	67	6
115-1237-1B 2 3 4	3634	Porocel 20 x 50 Mesh	1% Mo	Engelhard Commercial	Bachaquero Export Vacuum Residuum	775	1930	.52	6280	.024	12.7	1.87	216	49	6
						774	2000	.48	6440	.072	15.5	1.50	206	48	6
						778	2015	.51	5100	.111	16.1	1.52	199	49	4
						778	2000	.49	5570	.148	16.4	1.41	172	46	7
115-1238-1B 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20	3634	Porocel 20 x 50 Mesh	1% Mo	Engelhard Commercial	Bachaquero Export Vacuum Residuum	792	2010	.50	4320	.031	16.0	1.50	149	40	3
						790	2005	.51	4240	.069	16.1	1.38	161	45	7
						791	2000	.51	4780	.107	15.5	1.35	175	49	8
						790	2000	.51	4500	.145	14.9	1.41	186	55	2
						789	2000	.53	3750	.185	15.6	1.40	180	50	5
						789	1990	.53	4250	.225	15.0	1.37	189	52	6
						792	2005	.52	4150	.264	12.5	1.37	188	52	6
						790	2015	.51	4190	.302	13.6	1.39	177	51	4
						790	2000	.52	4430	.341	15.1	1.37	175	51	4
						790	2000	.51	4240	.379	15.0	1.43	183	51	5
						791	2000	.53	4220	.419	15.1	1.46	181	51	5
						790	2000	.51	4390	.457	15.0	1.36	187	50	6
						790	2010	.51	4090	.495	14.4	1.44	186	55	6
						790	2000	.50	3600	.532	15.9	1.33	184	55	10
						788	2010	.51	4290	.571	15.7	1.38	199	49	9
						790	2000	.51	3960	.609	13.7	1.34	203	49	9
						790	2015	.49	3920	.646	15.4	1.35	209	50	8
						790	2020	.48	4580	.682	16.0	1.38	207	49	10
						790	2000	.51	4190	.720	15.8	1.33	214	51	8
						791	2010	.51	4200	.758	15.6	1.52	219	52	7

Table A SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Catalyst Promoter	Preparation	Feed	Temp. °F	H ₂ Pres. psig	Space Velocity V/Hr/Nr	Space Velocity B/D/Lb	H ₂ Rate SCF/Lb	Cat. Age Bbl/Lb	Product Inspections				IBP- 550°F V %
												Gravity °API	% S	V ppm	Ni ppm	
115-1239-18	3634	Porocel 20 x 50 Mesh	1% Mo	Engelhard Commercial	Bachaquero Export Vacuum Residium L-397	790	2010	.52	.039	4450	.030	16.0	1.40	137	37	8
						790	2000	.51	.039	4620	.069	16.5	1.51	158	44	8
						793	2005	.50	.038	4560	.107	17.2	1.24	136	41	10
						790	2030	.48	.037	4680	.144	16.4	1.51	250	46	12
						790	2000	.50	.038	4190	.182	16.8	1.24	214	45	11
						790	2010	.50	.038	3970	.220	17.5	1.29	203	44	9
						790	2015	.50	.038	3880	.258	16.8	1.39	202	46	9
						789	1995	.51	.039	3500	.297	16.5	1.33	205	46	9
						789	1985	.52	.039	4050	.336	16.0	1.53	201	49	8
						790	2000	.49	.038	3920	.374	16.7	1.21	209	49	9
						790	2000	.50	.038	4590	.424	16.2	1.23	218	51	6
						790	2000	.49	.038	4130	.462	16.8	1.32	213	49	7
						790	1990	.43	.033	4050	.495	17.1	1.28	206	52	9
						790	1990	.35	.026	4720	.521	17.6	1.18	163	46	9
						792	1990	.36	.028	4300	.549	18.1	1.19	157	44	8
						790	1990	.34	.026	4450	.575	17.5	1.14	157	45	12
						790	1990	.34	.026	5030	.601	16.5	1.13	161	45	13
						790	1990	.35	.027	4130	.628	17.4	1.13	162	45	13
						790	2000	.33	.026	5660	.654	17.2	1.21	173	45	18
						791	2000	.35	.027	4740	.681	17.4	1.52	283	53	12
						790	2010	.34	.026	4640	.707	16.6	1.51	284	52	16
						792	2000	.36	.027	5340	.734					
115-1240-18	3634	Porocel 20 x 50 Mesh	1% Mo	Engelhard Commercial	Bachaquero Export Vacuum Residium	789	1990	.30	.023	6170	.016	17.5	.99	84	27	11
						790	1975	.29	.022	4840	.039	18.6	.87	62	25	12
						790	2000	.30	.022	5220	.061	17.9	.89	81	31	12
						790	1995	.29	.022	5040	.083	18.4	.90	99	35	11
						790	1990	.30	.023	4310	.106	18.1	1.00	98	34	11
						790	2000	.29	.022	5070	.128	18.4	.93	96	34	12
						790	2000	.30	.023	5670	.151	18.3	.94	109	36	12
						791	2005	.30	.023	4570	.174	16.8	.98	102	38	14
						790	2010	.29	.022	5080	.196	16.9	.98	95	38	13

Table A SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Catalyst Promoter	Preparation	Feed	Temp. °F	H ₂ Pres. psig	Space V-locity V/hr/Vr	H ₂ Rate SCF/Bbl	Cat. Age Bbl/Lb	Gravity °API	Product Inspections				IBP- 550°F V %
												% S	V ppm	M ppm		
115-1241-18 2 3 4 5	3634	Porocel 20 x 50 Mesh	1% Mo	Engelhard Commercial	Bachaquero Export Vacuum Residium	789	2000	.35	.026	.018	17.9	1.12	76	26		8
						790	2015	.31	.024	.042	19.0	.89	75	26		15
						789	2015	.32	.024	.066	17.9	.94	87	30		10
						790	1995	.32	.024	.090	18.5	.97	91	30		11
						789	2000	.33	.025	.103	17.6	1.04	99	35		12
115-1242-18 2 3 4 5 6A 6B 7 8	3634	Porocel 20 x 50 Mesh	1% Mo	Engelhard Commercial	Bachaquero Export Vacuum Residium	791	2000	.53	.040	.021	18.0	1.11	84	28		8
						791	1980	.30	.023	.044	19.8	.83	64	27		12
						788	2000	.30	.022	.066	17.5	.87	89	31		13
						790	2005	.28	.021	.087	18.2	.78	92	32		12
						789	2010	.29	.022	.109	17.0	1.02	100	32		13
						790	2010	.34	.026	.207	17.6	1.52				10
						790	2005	.31	.023	.294	17.7	1.13				15
						790	2000	.31	.023	.317						
115-1243-18 2 3 4	3634	Porocel 20 x 50 Mesh	1% Mo	Engelhard Commercial	Bachaquero Export Vacuum Residium	791	2005	.31	.023	.018	18.4	1.07	103	28		11
						791	2005	.31	.023	.041	18.7	.88	79	29		12
						790	2010	.31	.024	.065	18.2	.97	88	30		13
						790	2000	.30	.023	.077	16.9	1.00	104	32		11
115-1244-18 2 3 4 5 6 7 8	3634	Porocel 20 x 50 Mesh	1% Mo	Engelhard Commercial	Bachaquero Export Vacuum Residium	769	1990	.25	.019	.024	17.6	1.09				9
						770	2000	.25	.019	.043	16.8	.99	120	33		9
						770	1995	.25	.019	.062	17.2	1.09	118	35		11
						770	2000	.25	.019	.081	16.7	1.07	124	35		9
						770	1985	.25	.019	.100	16.5	1.15	152	43		10
						770	1975	.25	.019	.119	17.2	1.11	143	42		8
						780	1990	.25	.019	.138	17.1	1.00	131	41		10
						780	2000	.25	.019	.157	17.1	.88	118	44		10

* After Period 5, the Unit was on Wash for 8 hours.

Table A SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Catalyst Promoter	Preparation	Feed	Temp. °F	H ₂ Pres. psig	Space Velocity V/Hr/Vr	H ₂ Rate SCF/Bbl	Cat. Age Bbl/Lb	Gravity °API	Product Inspections				IBP- 550°F V %
												z S	V ppm	NI ppm		
115-1248-18	3634	Porocel 20 x 50 Mesh	1 %	Engelhard Commercial	Lloydalnster Vacuum Residuum HRI 3744	792	2020	1.54	3970	.069	13.3	2.12	46	51		4
						791	2020	1.50		.125						
						791	2020	1.49	3770	.181	13.6	2.15	42	47		8
						788	2010	1.65		.243						
						788	2010	1.87	4300	.313	15.2	2.61	57	48		4
						791	2000	1.93		.385						
						791	2000	1.86	3870	.455	15.5	2.42	58	49		8
						791	2000	1.93		.527						
						790	2000	1.98	4640	.601	16.5	2.63	62	48		4
						792	1950	2.09		.679						
						792	1950	2.06	4200	.756	13.8	2.71	61	61		8
						790	2010	2.03	4320	.833						
						791	2000	2.02		.985						
115-1249-18	3634	Porocel 20 x 50 Mesh	1 %	Engelhard Commercial	Lloydalnster Vacuum Residuum	791	2000	2.00	4240	1.060	12.7	2.76	67	47		8
						789	2000	1.97		1.134						
						789	2000	2.00	4240	1.209	12.8	2.92	67	55		6
						790	2015	.80	3700	.043	16.7	1.50	22	25		6
						789	2000	.77	4110	.102	17.5	1.45	24	30		6
						791	2010	.77	4660	.161	16.8	1.40	20	29		9
						774	2010	.77		.220	16.1	1.73	36	33		6
						792	2000	.77	4170	.279	15.9	1.68	35	33		8
						786	2000	.78	4550	.339	17.4	1.27	34	33		6
						786	1995	.76	4150	.397	16.5	1.73	31	32		5
						788	1990	.63	3650	.445	17.6	1.64	27	31		7
						791	1985	.62	4260	.493	17.7	1.59	21	31		7
						791	1980	.62	4190	.541	17.0		20	29		7
						790	2000	.63	5160	.589	15.7	1.82	30	37		5
						791	2000	.67	4320	.640	16.1	1.79	27	39		7
						792	2025	.67	5630	.691	15.8	1.88	39	43		8

DEMETALLIZATION

Table A-1. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1233-5B
Catalyst Age, BBL/LB	0.59
Feed	Bachaquero Export Vacuum Residuum
HRI Identification No.	L-397
Catalyst	(7.6 °API, 3.08 W% S) Engelhard Commercial (20 x 50 Mesh Porocel - 1% Mo)
HRI No.	

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	790
Liquid Space Velocity, $V_F/Hr/V_R$	1.46
Catalyst Space Velocity, B/D/LB	0.11
Reactor Type	Two-Stage Downflow
Hydrogen Rate, SCF/BBL	3950
Hydrogen Consumption, SCF/BBL	320
975°F+ Conversion, V %	14.3

YIELDS	W %	V %
H ₂ S & NH ₃	1.07	
C ₁ -C ₃	0.23	
C ₄ -650°F	4.35	5.24
650-975°F	18.17	19.67
975°F+	76.66	77.17
Total	100.48	
C ₄ +	99.17	102.08
Gravity, °API		11.7
Sulfur, W %	2.07	

FRACTION, °F	Coll. Liq.	18P- 650°F	650°F+ 650°F	650- 975°F	975°F+ 975°F	975- 1050°F	1050°F+ 1050°F
V % on Collected Liquid	100	5.0	95	19.3	75.7	9.52	66.18
Gravity, °API	11.6	34.5	10.4	19.2	8.0	18.8	7.3
Sulfur, W %	2.02	0.37	2.13	1.18	2.37	1.30	2.37
Carbon, W %	86.23						
Hydrogen, W %	11.05						
H/C Atomic Ratio	1.53						
Nitrogen, ppm	5394						
Aniline Point, °F				179			
Flash Point, °F			550				
Pour Point, °F			65				
RCR, W %	16.8				20.2		22.1
Vanadium, ppm	292						453
Nickel, ppm	46						90
Viscosity, SFS @210°F			438				
SFS @250°F			103				
Asphaltenes, W %							
Sulfur, W %	3.93						
Vanadium, ppm	269						
Nickel, ppm	70						
Asphaltene - free oil							
Vanadium, ppm	30						
Nickel, ppm	12						

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DEMETALLIZATION

Table A-2. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1238-4
Catalyst Age, BBL/LB	0.14
Feed	Bachaquero Export Vacuum Residuum
HRI Identification No.	L-397
	(7.6 °API, 3.07 W % S)
Catalyst	Engelhard Commercial
	(20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	790
Liquid Space Velocity, V/Hr/V	0.51
Catalyst Space Velocity, B/D/LB	0.04
Reactor Type	Two-stage-Downflow
Hydrogen Rate, SCF/BBL	4500
Hydrogen Consumption, SCF/BBL	400
975 °F + Conversion, V %	18.7

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H ₂ S & NH ₃	2.00	
C ₁ -C ₃	1.58	
C ₄ -650°F	7.20	8.88
650-975°F	18.50	20.33
975°F+	71.31	73.17
Total	100.59	102.38
C ₄ +	97.01	
Gravity, °API		15.3
Sulfur, W %	1.30	

<u>FRACTION, °F</u>	<u>Coll.</u> <u>Liq.</u>	<u>IBP-</u> <u>650°F</u>	<u>650°F+</u>	<u>650-</u> <u>975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	8.0	92.0	20.0	72.0
Gravity, °API	14.9	35.1	11.6	20.2	10.2
Sulfur, W %	1.41	0.13	1.81	0.67	1.57
Carbon, W %	87.75				
Hydrogen, W %	11.21				
H/C Atomic Ratio	1.52				
Nitrogen, ppm	4878				
Aniline Point, °F		140		172	
Flash Point, °F			535		
Pour Point, °F			70		
RCR, W %					
Vanadium, ppm					18.6
Nickel, ppm	186				
	55				
Bromine No., cgs/gm		10.5			
Viscosity, SFS @210°F			130		
SFS @250°F			49		

DEMETALLIZATION

Table A-3. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1238-14
Catalyst Age, BBL/LB	0.53
Feed	Bachaquero Export Vacuum Residuum
HRI identification No.	L-397
Catalyst	(7.6 °API, 3.08 W % S) Engelhard Commercial (20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	790
Liquid Space Velocity, $V_F/Hr/V_R$	0.50
Catalyst Space Velocity, B/D/LB	0.04
Reactor Type	Two-Stage Downflow
Hydrogen Rate, SCF/BBL	3600
Hydrogen Consumption, SCF/BBL	620
975°F+ Conversion, V %	16.6

YIELDS

	<u>W %</u>	<u>V %</u>
H ₂ S & NH ₃	2.00	
C ₁ -C ₃	1.45	
C ₄ -650°F	8.03	9.97
650-975°F	16.50	18.51
975°F+	72.95	75.07
Total	100.93	
C ₄ +	97.48	103.55
Gravity, °API	16.3	
Sulfur, W %	1.32	

FRACTION, °F

	<u>Coll.</u>	<u>IBP-</u>	<u>650°F</u>	<u>650°F+</u>	<u>650-</u>	<u>975°F</u>	<u>975°F+</u>
	<u>Liq.</u>	<u>650°F</u>	<u>650°F</u>	<u>650°F+</u>	<u>975°F</u>	<u>975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	9.0	91.0	18.0	73.0		
Gravity, °API	15.9	36	14.2	23.4	10.2		
Sulfur, W %	1.33	0.16	1.45	0.64	1.61		
Carbon, W %	86.15						
Hydrogen, W %	11.28						
H/C Atomic Ratio	1.56						
Nitrogen, ppm	4364						
Bromine No., cgs/gm		8.5					
Aniline Point, °F		140			173		
Flash Point, °F			515				
Pour Point, °F			60				
RCR, W %							18.4
Vanadium, ppm	184						
Nickel, ppm	55						
Viscosity, SFS @250°F			44				

DEMETALLIZATION

Table A-4. OPERATING CONDITIONS, YIELDS AND PRODUCT PROPERTIES

Run Number	115-1240-3
Catalyst Age, BBL/LB	0.06
Feed	Bachaquero Export Vacuum Residuum
HRI Identification No.	L-397
Catalyst	(7.6 °API, 3.08 W %) Engelhard Commercial
HRI No.	(20 x 50 Mesh Porocel - 1% Mo) 3634
<u>OPERATING CONDITIONS</u>	
Hydrogen Pressure, psig	2000
Temperature, °F	790
Liquid Space Velocity, $V_F/Hr/V_R$	0.3
Catalyst Space Velocity, B/D/LB	0.02
Reactor Type	Two-Stage Downflow
Hydrogen Rate, SCF/BBL	5220
Hydrogen Consumption, SCF/BBL	720
975°F+ Conversion V %	29.3

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H ₂ S & NH ₃	2.46	
C ₁ -C ₃	0.53	
C ₄ -650°F	13.50	15.54
650-975°F	22.99	25.47
975°F+	61.58	63.61
Total	101.06	
C ₄ +	98.08	105.62
Gravity, °API		18.3
Sulfur, W %	0.97	

<u>FRACTION, °F</u>	<u>Coll. Liq.</u>	<u>IBP- 650°F</u>	<u>650°F+</u>	<u>650- 975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	15.0	85.0	24.3	60.7
Gravity, °API	17.9	35.5	15.2	21.5	11.2
Sulfur, W %	0.89	0.07	1.12	0.59	1.30
Carbon, W %	86.50				
Hydrogen, W %	11.54				
H/C Atomic Ratio	1.59				
Nitrogen, ppm	3467				
Bromine No., cgs/gm		9.4			
Aniline Point, °F		140		170	
Flash Point, °F			485		
Pour Point, °F			40		
RCR, W %					17.8
Vanadium, ppm	81				122
Nickel, ppm	31				46
Viscosity, SFS @ 122°F			1420		
-SFS @ 210°F			57		230

DEMETALLIZATION

Table A-5. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1240-8
Catalyst Age, BBL/Lb	0.17
Feed	Bachaquero Export Vacuum Residuum
HRI Identification No.	L-397
	(7.6 °API, 3.08 W % S)
Catalyst	Engelhard Commercial
	(20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	791
Liquid Space Velocity, V _F /Hr/V _R	0.30
Catalyst Space Velocity, B/D/LB	0.02
Reactor Type	Two-Stage Downflow
Hydrogen Rate, SCF/BBL	4570
Hydrogen Consumption, SCF/BBL	634
975°F+ Conversion, V %	32.11

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H ₂ S & NH ₃	2.28	
C ₁ -C ₃	0.52	
C ₄ -650°F	11.93	14.66
650-975°F	26.25	29.15
975°F+	59.96	61.10
Total	100.94	
C ₄ +	98.13	104.91
Gravity, °API		17.2
Sulfur, W %	0.98	

<u>FRACTION, °F</u>	<u>Coll.</u>	<u>18P-</u>	<u>650-</u>	<u>650-</u>	<u>650-</u>	<u>975°F+</u>
	<u>Liq.</u>	<u>650°F</u>	<u>650°F+</u>	<u>975°F</u>	<u>975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	13.3	86.7	28.0		58.7
Gravity, °API	16.8	35.5	13.7	21.6		9.0
Sulfur, W %	0.98	0.13	1.25	0.57		1.36
Carbon, W %	86.24					
Hydrogen, W %	11.41					
H/C Atomic Ratio	1.58					
Nitrogen, ppm	4585					
Bromine No., cgs/gm		13.2				
Aniline Point, °F		142			168	
Flash Point, °F			510			
Pour Point, °F			55			
RCR, W %						19.1
Vanadium, ppm	102					
Nickel, ppm	38					
Viscosity, SFS @122°F			1587			
SFS @210°F			60			425

DEMETALLIZATION

Table A-6. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1248-98
Catalyst Age, BBL/LB	1.21
Feed	Lloydminster Vacuum Residuum
HRI Identification No.	3744
	(6.4 °API, 5.4 W % S)
Catalyst	Engelhard Commercial
	(20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	789
Liquid Space Velocity, V _F /Hr/V _R	2.00
Catalyst Space Velocity, B/D/LB	0.15
Reactor Type	Two-stage Downflow
Hydrogen Rate, SCF/BBL	4240
Hydrogen Consumption, SCF/BBL	420
975°F+, Conversion, V %	16.6

<u>YIELDS</u>	<u>W %</u>		<u>V %</u>
H ₂ S & NH ₃	2.99		
C ₁ -C ₃	0.49		
C ₄ -650°F	5.74		6.95
650-975°F	26.23		28.74
975°F+	65.17		66.01
Total	100.62		
C ₄ +	97.14		101.70
Gravity, °API		12.9	
Sulfur, W %	2.92		

<u>FRACTION, °F</u>	<u>Coll.</u>	<u>1BP-</u>		<u>650-</u>		<u>975°F+</u>
	<u>Liq.</u>	<u>650°F</u>	<u>650°F+</u>	<u>975°F</u>		
V % on Collected Liquid	100	6.7	93.3	28.3		65.0
Gravity, °API	12.8	32.8	10.2	18.0		6.7
Sulfur, W %	2.92	0.72	3.05	1.45		3.67
Carbon, W %	85.57					
Hydrogen, W %	11.05					
H/C Atomic Ratio	1.54					
Nitrogen, ppm	4080					
Aniline Point, °F		131		163		
Flash Point, °F			510			
Pour Point, °F			65			
RCR, W %						16.9
Vanadium, ppm	67					
Nickel, ppm	55					
Viscosity, SFS @210°F			144			

DEMETALLIZATION

Table A-7. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1249-9
Catalyst Age, BBL/LB	0.49
Feed	Lloydminster Vacuum Residuum
HRI Identification No.	3744
	(6.4 °API, 5.4 W % S)
Catalyst	Engelhard Commercial
	20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

OPERATING CONDITIONS

Hydrogen Pressure, psig	1980
Temperature, °F	791
Liquid Space Velocity, $V_F/Hr/V_R$	0.62
Catalyst Space Velocity, B/D/LB	0.05
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3960
Hydrogen Consumption, SCF/BBL	640
975°F+ Conversion, V %	30.9

YIELDS

	<u>W %</u>	<u>V %</u>
H ₂ S & NH ₃	4.46	
C ₁ -C ₃	0.54	
C ₄ -650°F	10.97	13.63
650-975°F	33.17	35.57
975°F+	51.80	34.65
Total	100.94	
C ₄ +	95.94	103.86
Gravity, °API		17.8
Sulfur, W %	1.59	

<u>FRACTION, °F</u>	<u>Coll.</u>	<u>IBP-</u>	<u>650°F</u>	<u>650°F+</u>	<u>650-</u>	<u>975°F</u>	<u>975°F+</u>
	<u>Liq.</u>	<u>650°F</u>	<u>650°F+</u>	<u>650°F+</u>	<u>975°F</u>	<u>975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	13	87	34.3	52.7		
Gravity, °API	17.7	32.9	10.8	19.7	8.5		
Sulfur, W %	1.59	0.14	1.63	0.74	2.27		
Carbon, W %	86.13						
Hydrogen, W %	11.35						
H/C Atomic Ratio	1.57						
Nitrogen, ppm	3360						
Aniline Point, °F		137		167			
Flash Point, °F			475				
Pour Point, °F			60				
RCR, W %						17.2	
Vanadium, ppm	21						
Nickel, ppm	31						
Viscosity, SFS @210°F			42				

Table B SUMMARY OF DESULFURIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. °F	Hydrogen Pressure psig	Space Velocity V/Hr/Vr	Hydrogen Rate SCF/Hr	Catalyst Age Bbl/lb	Gravity API	Product % S	Product V ppm	Product Inspections Ni ppm	IBP-550°F V T
184-194-18	3104	Amer. Cy. 0.02" Beads	Bachaquero Export Vacuum Residuum L-100	Comm. Demet. Catalyst HRI 3634	756	1960	1.13	4500	.083	14.2	1.31	230	43	1
2					760	2025	1.06	4460	.196	15.5	.69	240	44	6
3					761	2005	1.03	4400	.306	15.5	.68	236	42	4
4					761	2000	1.00	4210	.413	15.3	.80	231	42	4
5					762	2010	.95	4400	.514	15.1	.69	229	47	6
6					760	2000	.99	4820	.619	14.9	.75	248	48	2
7					761	2000	1.02	4690	.728	14.7	.75	248	49	1
8					762	1990	1.05	4150	.840	15.7	.82	245	49	1
9					760	1975	.94	4260	.940	15.5	.82	215	47	1
10					759	1990	1.04	4270	1.051	16.4	.82	216	47	3
11					760	1950	1.05	4270	1.163	16.4	.83	217	47	1
12					760	1985	1.03	5080	1.273	15.9	.84	220	47	1
13					763	2000	1.15	4190	1.396	16.2	.83	221	46	1
14					762	2000	1.11	4270	1.515	16.2	.91	260	50	1
15					762	2000	1.05	4780	1.627	16.6	.93	253	54	4
16					751	2000	1.02	4820	1.736	16.5	.97	254	54	1
17					760	2000	1.05	3950	1.848	16.3	.90	254	54	1
18					759	1995	1.10	3900	1.966	16.0	.86	254	59	1
19					757	2010	1.04	3900	2.077	15.5	.91	260	59	2
20					756	2025	1.07	4270	2.191	14.0	.91	263	54	5
184-195-18	3104	Amer. Cy. 0.02" Beads	Bachaquero Export Vacuum Residuum L-401	Comm. Demet. Catalyst HRI 3634	761	2020	1.19	3860	.110	16.9	.59	148	39	4
2					759	2010	1.22	3660	.241	17.5	.64	155	40	6
3					761	2000	1.11	4340	.360	17.0	.63	154	41	6
4					761	2005	1.07	4310	.474	16.7	.69	153	45	8
5					760	2000	1.01	3710	.582	16.3	.67	153	45	7
6					761	1990	1.11	4050	.701	15.8	.59	158	40	5
7					759	2010	0.99	4430	.807	15.9	.57	152	41	9
8					762	2020	1.12	3580	.927	16.8	.64	169	40	6
9					761	2025	1.05	4980	1.039	16.6	.66	168	41	5
10					761	2015	1.03	4910	1.149	16.7	.65	168	41	5
11					760	2005	1.06	4050	1.262	17.2	.65	161	38	4
12					762	2010	1.03	4660	1.372	16.7	.68	161	38	6
13					762	2000	1.09	3980	1.489	15.8	.59			6
14					760	2005	1.05	4030	1.601	17.6	.69			5
15					758	2010	1.06	4280	1.714	17.4	.68			6
16					760	2025	.97	4360	1.817	17.8	.71	159	37	6
17					761	2000	1.05	4300	1.929	17.2	.60			5
18					759	2005	1.12	3880	2.049	17.4	.63			5
19					762	2010	.93	5110	2.148	17.1	.64	164	39	5
20					760	1985	1.16		2.272	16.4	.68			4

Table 8 SUMMARY OF DESULFURIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. °F	Hydrogen Pressure psig	Space Velocity V/Hr/Vr	Hydrogen Rate SCF/Bbl	Catalyst Age Bbl/Lb	Gravity °API	Product Inspections			
											Σ S	V ppm	Ni ppm	18P-550°F V %
184-196-18	3104	Amer. Cy. 0.02" Beads	Bachaquero Export Vacuum Residium L-405	Comm. Demet. Catalyst HRI 3634	760	1950	.32	4970	.029	20.6	.45	95	25	9
2					760	2010	.57	3980	.089	19.2	.45	118	27	8
3					760	2000	.54	4390	.146	18.5	.38	118	30	12
4					762	2000	.53	3860	.203	19.4	.37	124	29	9
5					760	2010	.53	3810	.258	20.2	.45	129	35	9
6					759	2000	.52	4150	.313	19.6	.43	133	35	7
7					760	1995	.55	3730	.371	23.7	.51	130	39	10
8					760	2000	.53	4220	.424	19.2	.44	131	39	12
9					759	2000	.54	4200	.478	19.8	.39	142	40	11
10					760	1990	.54	4400	.532	19.8	.37	144	39	9
11					762	2010	.52	3780	.584	21.1	.39	135	37	10
12					760	2000	.53	4560	.637	19.4	.38	143	35	13
13					760	2010	.52	4050	.692	19.3	.37	146	34	10
14					761	2000	.49	4710	.744	19.9	.35	142	36	9
15					760	1995	.54	4620	.801	20.0	.41	145	35	9
16					761	2020	.50	4440	.854	19.7	.36	145	37	10
17					760	1995	.55	4280	.909	18.6	.40	148	37	12
18					760	2000	.57	4220	.969	19.0	.45	150	38	9
19					759	2000	.56	4310	1.028	18.0	.44	158	37	9
20					760	1995	.57	4530	1.088	19.3	.48	160	38	11
184-197-18	3104	Amer. Cy. 0.02" Beads	Bachaquero Export Vacuum Residium L-405	Comm. Demet. Catalyst HRI 3634	780	2000	.58	3650	.041	20.9	.27			12
2					779	2000	.56	4140	.100	21.0	.29	96	26	11
3					782	2010	.57	3530	.160	19.7	.33	111	30	10
4					781	2010	.54	4280	.217	19.6	.31	118	30	13
5					779	2010	.55	4310	.275	20.5	.33	120	32	13
6					781	2010	.52	4140	.330	20.7	.34	126	32	14
7					749	2000	.58	4080	.384	20.0	.51	148	36	14
8					782	1990	.62	3310	.449	20.9	.42	146	137	13
9							.57		.454					
184-198-18	3104	Amer. Cy. 0.02" Beads	Bachaquero Export Vacuum Residium L-406	Comm. Demet. Catalyst HRI 3634	770	1990	.46	5400	.038	21.7	.40			12
2					772	2000	.46	4050	.086	21.7	.31	99	29	13
3					771	2000	.49	3590	.137	21.5	.33	106	29	15
4					767	2000	.47	1850	.172	20.4	.65	106	30	13

Table B SUMMARY OF DESULFURIZATION RUNS

Run No.,-Period	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. °F	Hydrogen Pressure psig	Space Velocity V/Hr/Nr B/D/Lb	Hydrogen Rate SCF/Bbl	Catalyst Age Bbl/Lb	Product Inspections		
										Gravity °API	% S	V ppm
185-248-18	3104	Amer. Cy. 0.02" Beads	Bachaquero Export Vacuum Residium L-406	Comm. Demet. Catalyst HRI 3634	780	1970	.56	.059	.039	22.0	.24	63
185-249-18	3104	Amer. Cy. 0.02" Beads	Bachaquero Export Vacuum Residium L-408	Comm. Demet. Catalyst HRI 3634	763	2020	1.21	.129	.084	19.7	.56	63
185-250-18	3104	Amer. Cy. 0.02" Beads	Lloydminster Vacuum Residium L-422	Comm. Demet. Catalyst HRI 3634	760	2015	1.00	.107	.100	15.0	.79	40

IBP-550°F

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Table B SUMMARY OF DESULFURIZATION RUNS

Run No.-Perio.	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. F	Hydrogen Pressure psig	Space Velocity V/Hr/Vr B/D/Lb	Hydrogen Rate SCF/Bbl	Catalyst Age Bbl/Lb	Gravity API	Product Inspections % S V ppm MI ppm V %
185-250-7	3104	Amer. Cy. 0.02" Beads	Lloydminster Vacuum Residue L-422	Comm. Demet. Catalyst HRI 3634	759	1960	1.25	7040	.818	18.4	.73 40 31 4
8					760	1985	1.08	5650	.933	18.2	.68 39 30 4
9					755	2010	.94	4350	1.033	19.0	.68 38 30 4
10					755	2020	.87	5410	1.126	17.1	.73 3 3
11					760	2015	1.16	4460	1.250	17.1	.79 49 33 5
12					752	2000	1.27	3220	1.386	16.8	.92 4 4
13					760	1995	.88	5000	1.480	17.9	.70 4 4
14					764	2005	1.21	3610	1.610	17.6	.69 43 34 4
15					759	2005	1.10	3930	1.728	18.2	.75 40 34 4
16					760	1995	1.15	3770	1.851	17.6	.78 3 3
17					759	2000	1.00	4340	1.958	16.7	.72 50 31 4
18					761	2010	.99	4420	2.064	17.6	.65 49 30 4
19					760	1995	1.00	4500	2.171	17.9	.71 50 30 2
20					766	2010	1.23	3830	2.303	15.9	.80 3 3
21					766	2015	1.23	3720	2.435	17.6	.81 46 33 4
22					770	2010	1.19	3920	2.562	17.1	.82 1 1
23					760	2000	1.01	4270	2.670	18.4	.72 38 29 4
24					758	1985	1.06	4560	2.783	17.9	.79 44 32 4
25					758	1980	1.04	5150	2.894	17.2	.85 45 33 4
26					759	1995	.93	5110	2.994	17.9	.79 45 32 4
185-251-18	3104	Amer. Cy. 0.02" Beads	Lloydminster Vacuum Residue L-424	Comm. Demet. Catalyst HRI 3634	758	2000	1.18	4230	.130	18.3	.58 4 4
2					757	2000	1.15	4150	.252	19.4	.59 12 21 3
3					761	2015	1.14	4450	.373	19.3	.40 12 22 4
4					760	2005	1.11	4730	.491	18.9	.49 18 16 4
5					761	2000	1.18	5290	.620	19.2	.55 18 16 4
6					761	2010	1.06	4300	.732	19.4	.47 17 19 5
7					759	1995	1.11	4110	.850	18.9	.50 16 20 5
8					761	1995	1.24	3900	.981	18.4	.53 16 20 6
9					760	2000	1.20	3710	1.108	18.7	.65 18 20 5
10					761	2000	1.21	3660	1.236	18.0	.61 20 20 5
11					760	2005	1.12	3990	1.355	18.6	.66 20 22 5
12					761	1990	1.01	5090	1.462	18.9	.45 20 20 3
13					759	2000	1.05	3760	1.573	18.5	.57 21 21 6
14					760	1990	1.15	3980	1.695	19.1	.54 4 4
15					760	1980	1.30	3620	1.833	18.2	.61 18 21 5

Table B SUMMARY OF DESULFURIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. °F	Hydrogen Pressure psig	Space Velocity V/Hr/Vr	Hydrogen Rate SCF/Hr	Catalyst Age Bbl/Lb	Gravity °API	Product Inspections V ppm	NI ppm	IBP-550°F V %
185-251-16	3104	Amer. Cy. 0.02% Beads	Lloydminster Vacuum Residue L-424	Comm. Demet. Catalyst HRI 3634	760	1980	1.21	3340	1.561	18.3	.69		4
17					761	1990	1.16	3780	2.083	18.7	.58	23	4
18					761	2000	1.09	4540	2.198	18.7	.64		6
19					758	1990	1.15	5100	2.320	18.6	.64	24	6
20					761	1990	1.13	3670	2.440	18.5	.59	20	5
21					760	1995	1.20	3550	2.567	18.5	.64		6
22					759	1980	1.08	3740	2.681	18.0	.73	24	5
23					760	1995	1.08	4150	2.795	19.6	.70		6
24					760	2000	1.13	3250	2.915	18.8	.65	25	5

DESULFURIZATION

Table B-1. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-194-17
Catalyst Age, BBL/LB	1.85
Feed	Demetallized Bachaquero Export
	Vacuum Residuum
HRI Identification No.	L-400
	(11.3 °API, 1.98 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	760
Liquid Space Velocity, V _F /Hr/V _R	1.05
Catalyst Space Velocity, B/D/LB	0.112
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3950
Hydrogen Consumption, SCF/BBL	365
975°F+ Conversion, V %	9.2

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H ₂ S & NH ₃	1.23	
C ₁ -C ₃	1.07	
C ₄ -650°F	6.98	8.38
650°F-975°F	21.60	23.55
975°F	69.67	70.15
Total	100.55	
C ₄ +	98.25	102.08
Gravity, °API		16.9
Sulfur, W %	0.89	

<u>FRACTION, °F</u>	<u>Coll.</u>	<u>IBP-</u>	<u>650-</u>	<u>650-</u>	<u>975°F+</u>
<u>Liq.</u>	<u>650°F</u>	<u>650°F+</u>	<u>975°F</u>		
V % on Collected Liquid	100	7.3	92.7	23.3	69.4
Gravity, °API	16.3	32.1	14.4	22.9	11.1
Sulfur, W %	0.90		1.03	0.13	1.22
Carbon, W %	86.92				
Hydrogen, W %	11.54				
Nitrogen, ppm	3735				
Aniline Point, °F		137		155	
Flash Point, °F			535		
Pour Point, °F			50		
RCR, W %					16.7
Viscosity, SFS @210°F			124		

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DESULFURIZATION

Table B-2. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-195-4
Catalyst Age, BBL/LB	0.47
Feed	65-70% Demetallized Bachaquero Export
	Vacuum Residuum
HRI Identification No.	L-401
	(13.1 °API, 1.39 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	761
Liquid Space Velocity, V/Hr/V	1.07
Catalyst Space Velocity, B/D/LB	C.11
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4300
Hydrogen Consumption, SCF/BBL	310
975°F+ Conversion, V %	5.6

YIELDS	W %	V %
H ₂ S & NH ₃	0.92	
C ₁ -C ₃	0.40	
C ₄ -400°F	1.24	1.65
400-650°F	7.57	8.78
650-975°F	22.29	24.26
975°F+	68.06	68.92
Total	100.48	
C ₄ +	99.16	103.61
Gravity, °API		19.6
Sulfur, W %	0.67	

FRACTION, °F	Coll. Liq.	1BP-400°F	400°F+	400-650°F	650°F+	650-975°F	975°F+
V % on Collected Liquid	100	1.25	98.75	8.50	90.25	23.5	66.75
Gravity, °API	16.7	47.2	15.7	32.5	14.2	22.4	11.7
Sulfur, W %	0.69	<0.03	0.68	<0.03	0.72/0.69	0.15	0.92
Carbon, W %	86.34						
Hydrogen, W %	11.59						
H/C Atomic Ratio	1.60						
Nitrogen, ppm	3527						
Bromine No. cgs/gm		4.4		6.1			
Aniline Point, °F				141		177	
Flash Point, °F			360		510		
Pour Point, °F			25		60		
Smoke Point, °F							
ASTM Color				L-4.5			
RCR, W %							16.8
Vanadium, ppm	153						
Nickel, ppm	45						
Viscosity, SUS @210°F			364		693		
SFS @122°F			521		960		
SFS @210°F							330
SFS @250°F							114

DESULFURIZATION

Table B-3. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-195-19
Catalyst Age, BBL/LB	2.15
Feed	65-70% Demetallized Bachaquero Export
	Vacuum Residuum
HRI Identification No.	L-401
	(13.1 °API, 1.39 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2010
Temperature, °F	762
Liquid Space Velocity, V/Hr/V	0.93
Catalyst Space Velocity, B/O/LB	0.10
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	5110
Hydrogen Consumption, SCF/BBL	275
975°F+ Conversion, V %	9.7

YIELDS

	W %	V %
H ₂ S & NH ₃	1.12	
C ₁ -C ₃	0.40	
C ₄ -400°F	1.03	1.37
400-650°F	7.54	8.62
650-975°F	24.24	25.87
975°F+	66.09	65.91
Total	100.42	
C ₄ +	98.90	101.77
Gravity, °API	17.3	
Sulfur, W %	0.48	

FRACTION, °F	Coll. Liq.	1BP- 400°F	400°F+ 400°F+	400- 650°F	650°F+ 650°F+	650- 975°F	975°F+ 975°F+
V % on Collected Liquid	100	1.0	99.0	8.5	90.5	25.5	65.0
Gravity, ° API	17.1	49.4	15.6	32.9	14.2	22.0	12.0
Sulfur, W %	0.64	<0.03	0.49	<0.03	0.63	0.13	0.76
Carbon, W %	86.50						
Hydrogen, W %	11.59						
H/C Atomic Ratio							
Nitrogen, ppm	3540						
Bromine No. cgs/gm		3.7		5.9			
Aniline Point, °F				139		176	
Flash Point, °F			430		500		
Pour Point, °F			35		55		
Smoke Point, °F							
ASTM Color				6.0			
RCR, W %							15.9
Vanadium, ppm	164						
Nickel, ppm	39						
Viscosity, SUS @210°F			335		630		
SFS @122°F			644		956		
SFS @210°F							356
SFS @250°F							105

DESULFURIZATION

Table B-4. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-196-4
Catalyst Age, BBL/LB	0.20
Feed	65-70% Demetallized Bachaquero Export
	Vacuum Residuum
HRI Identification No.	L-405
	(14.4 °API, 1.40 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	762
Liquid Space Velocity, V _F /Hr/V _R	0.53
Catalyst Space Velocity, B/D/LB	0.06
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3860
Hydrogen Consumption, SCF/BBL	410
975°F+ Conversion, V %	8.0

YIELDS

	W %	V %
H ₂ S & NH ₃	1.35	
C ₁ -C ₃	0.40	
C ₄ -400°F	2.6	3.42
400-650°F	9.43	10.72
650-975°F	24.48	26.02
975°F+	62.32	62.25
Total	100.64	
C ₄ +	98.89	102.41
Gravity, °API		19.6
Sulfur, W %	0.34	

FRACTION, °F	Coll. Liq.	IBP-400°F	400°F+400°F	400-650°F	650°F+650°F	650-975°F	975°F+975°F
V % on Collected Liquid	100	3.0	97.0	10.5	86.5	25.5	61.0
Gravity, °API	19.4	50.4	18.5	33.2	15.7	22.5	13.2
Sulfur, W %	0.37	<0.03	0.33	<0.03	0.50	0.05	0.52
Carbon, W %	86.68						
Hydrogen, W %	11.77						
H/C Atomic Ratio	1.62						
Nitrogen, ppm	3316						
Bromine No. cgs/gm		4.1		6.7			
Aniline Point, °F		129		141		176	
Flash Point, °F			390		500		
Pour Point, °F			30		60		
Smoke Point, °F				11			
ASTM Color		L-2.5		5.0			
RCR, W %							14.9
Vanadium, ppm	124						
Nickel, ppm	29						
Viscosity, SUS @210°F			202		526		
SFS @122°F			180		582		
SFS @210°F					37		226
SFS @210°F							90

DESULFURIZATION

Table B-5. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-196-20
Catalyst Age, BBL/LB	1.09
Feed	65-70% Demetallized Bachaquero Export Vacuum Residuum
HRI Identification No.	L-405
Catalyst	(14.4 °API, 1.40 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	1990
Temperature, °F	760
Liquid Space Velocity, Vf/Hr/V _R	0.57
Catalyst Space Velocity, B/D/LB	0.06
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4530
Hydrogen Consumption, SCF/BBL	345
975°F+ Conversion, V %	16.6

YIELDS

	W %	V %
H ₂ S & NH ₃	1.20	
C ₁ -C ₃	0.40	
C ₄ -400°F	3.54	4.38
400-650°F	9.44	10.59
650-975°F	28.35	29.76
975°F+	57.60	56.49
Total	100.53	
C ₄ +	98.93	101.22
Gravity, °API		17.8
Sulfur, W %	0.48	

FRACTION, °F	Coll. Liq.	IBP-400°F	400°F+	400-650°F	650°F+	650-975°F	975°F+
V % on Collected Liquid	100	4.0	96.0	10.5	85.5	29.5	56.0
Gravity, ° API	19.3	47.3	17.2	33.2	15.3	22.5	12.4
Sulfur, W %	0.48		0.45		0.56	< 0.03	0.80
Carbon, W %	86.57						
Hydrogen, W %	11.67						
H/C Atomic Ratio	1.60						
Nitrogen, ppm	3322						
Bromine No. cgs/gm		2.6		5.8			
Aniline Point, °F		131		137		181	
Flash Point, °F			410		500		
Pour Point, °F			20		45		
Smoke Point, °F				12.0			
ASTM Color				L-5.0			
RCR, W %							16.5
Vanadium, ppm	160						
Nickel, ppm	38						
Viscosity, SUS @210°F			236		540		
SFS @122°F			195		650		
SFS @210°F							393
SFS @250°F							120

DESULFURIZATION

Table B-6. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-248-3
Catalyst Age, BBL/LB	0.15
Feed	65-70% Demetallized Bachaquero Export Vacuum Residuum
HRI Identification No.	L-406
Catalyst	(15.0 °API, 1.25 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	780
Liquid Space Velocity, V/Hr/V	0.56
Catalyst Space Velocity, B/D/LB	0.06
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4060
Hydrogen Consumption, SCF/BBL	480
975°F+ Conversion, V %	16.0

YIELDS

	W %	V %
H ₂ S & NH ₃	1.25	
C ₁ -C ₃	0.81	
C ₄ -400°F	5.33	6.82
400-650°F	12.21	13.84
650-975°F	27.40	29.24
975°F+	53.74	54.03
Total	100.74	
C ₄ +	98.69	103.93
Gravity, °API	22.8	
Sulfur, W %	0.37	

FRACTION, °F	Coll. Liq.	IBP-400	400°F+	400-650°F	650°F+	650-975°F	975°F+
V % on Collected Liquid	100	6.0	94.0	13.4	80.6	28.3	52.3
Gravity, °API	22.5	50.6	19.9	32.4	17.8	22.8	13.9
Sulfur, W %	0.28		0.31	0.04	0.40	0.12	0.61
Carbon, W %	86.41						
Hydrogen, W %	11.93						
H/C Atomic Ratio	1.64						
Nitrogen, ppm	2635						
Bromine No., cgs/gm		3.7		4.8			
Aniline Point, °F		128		141		180	
Flash Point, °F			365		480		
Pour Point, °F			35		45		
Smoke Point, °F				12.5			
ASTM Color		L-2.0		4.5			
RCR, W %							14.6
Vanadium, ppm	77						
Nickel, ppm	23						
Viscosity, SUS @210°F			117		272		
SFS @210°F							155

DESULFURIZATION

Table B-7. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-248-11
Catalyst Age, BBL/LB	0.63
Feed	65-70% Demetallized Bachaquero Export
	Vacuum Residuum
HRI Identification No.	L-406
	(15 °API, 1.25 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2010
Temperature, °F	780
Liquid Space Velocity, V/Hr/V	0.55
Catalyst Space Velocity, B/D/LB	0.06
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4300
Hydrogen Consumption, SCF/BBL	480
975°F+ Conversion, V %	26.7

YIELDS

	W %	V %
H ₂ S & NH ₃	1.33	
C ₁ -C ₃	0.71	
C ₄ -400°F	6.60	8.44
400-650°F	12.72	13.33
650-975°F	32.06	34.14
975°F+	47.27	47.16
Total	100.75	
C ₄ +	98.71	103.06
Gravity, °API		21.5
Sulfur, W %	0.30	

FRACTION, °F	Coll. Liq.	18P- 400°F	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	7.7	92.3	13.0	79.3	33.3	46.0
Gravity, ° API	21.2	49.9	20.1	32.4	17.6	22.6	12.9
Sulfur, W %	0.31		0.36	0.04	0.37		0.67
Carbon, W %	86.66						
Hydrogen, W %	11.98						
H/C Atomic Ratio	1.64						
Nitrogen, ppm	2487						
Bromine No., cgs/gm		3.1		4.6			
Aniline Point, °F		130		140		184	
Flash Point, °F			335		475		
Pour Point, °F			35		50		
Smoke Point, °F				13.0			
ASTM Color		0.5		L-3.5			
RCR, W %							15.49
Vanadium, ppm	76						
Nickel, ppm	28						
Viscosity, SUS @210°F			123		302		
SFS @210°F							308

DESULFURIZATION

Table B-8. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-249-4
Catalyst Age, BBL/LB	0.44
Feed	80-85% Demetallized Bachaquero Export Vacuum Residuum
HRI Identification No.	L-408
Catalyst	(17.5 °API, 1.00 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	760
Liquid Space Velocity, V/Hr/V	1.11
Catalyst Space Velocity, B/D/LB	0.12
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4360
Hydrogen Consumption, SCF/BBL	
975°F+ Conversion, V %	10.4

YIELDS

	W %	V %
H ₂ S & NH ₃	0.58	
C ₁ -C ₃	0.48	
C ₄ -400°F	1.56	1.94
400-650°F	10.42	11.53
650-975°F	28.10	29.13
975°F+	59.23	57.06
Total	100.37	
C ₄ +	99.31	99.66
Gravity, °API		18.0
Sulfur, W %	0.55	

FRACTION, °F	Coll. Liq.	18P-400°F	400°F+400°F	400-650°F	650°F+650°F	650-975°F	975°F+
V % on Collected Liquid	100	1.7	98.3	11.6	86.7	29.3	57.4
Gravity, ° API	17.9	49.4	18.7	32.6	14.9	22.2	11.4
Sulfur, W %	0.51		0.45	<0.02	0.59	0.19	0.82
Carbon, W %	86.30						
Hydrogen, W %	11.71						
H/C Atomic Ratio	1.62						
Nitrogen, ppm	3201						
Bromine No. cgs/gm		2.67		5.19			
Aniline Point, °F							
Flash Point, °F			410		490		
Pour Point, °F			20		35		
Smoke Point, °F				12.0			
ASTM Color							
RCR, W %							15.9
Vanadium, ppm	63						
Nickel, ppm	20						
Viscosity, SUS @210°F			165				
SFS @ 122°F			175				
SFS @ 210°F					745		
					34		184

DESULFURIZATION

Table B-9. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-249-15
Catalyst Age, BBL/LB	1.76
Feed	80-85% Demetallized Bachaquero Export
	Vacuum Residuum
HRI Identification No.	L-408
	(17.5 °API, 1.00 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	761
Liquid Space Velocity, V/Hr/V	1.07
Catalyst Space Velocity, B/D/LB	0.11
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4160
Hydrogen Consumption, SCF/BBL	
975°F+ Conversion, V %	10.7

YIELDS	W %	V %
H ₂ S & NH ₃	0.47	
C ₁ -C ₃	0.52	
C ₄ -400°F	1.64	1.90
400-650°F	10.78	11.98
650-975°F	28.25	29.25
975°F+	58.60	56.90
Total	100.25	
C ₄ +	99.27	100.08
Gravity, °API		18.7
Sulfur, W %	0.64	

FRACTION, °F	Coll. Liq.	IBP- 400°F	400°F+ 400°F+	400- 650°F	650- 650°F+	650- 975°F	975°F+ 975°F+
V % on Collected Liquid	100	1.7	98.3	12.0	86.3	29.3	57.0
Gravity, °API	18.6	39.2	17.9	32.8	16.9	21.5	12.0
Sulfur, W %	0.47		0.66	<0.02	0.55	0.21	0.97
Carbon, W %	86.84						
Hydrogen, W %	11.67						
H/C Atomic Ratio	1.60						
Nitrogen, ppm	3377						
Bromine No. cgs/gm		2.1		5.8			
Aniline Point, °F			140		165		
Flash Point, °F			320		480		
Pour Point, °F			25		40		
Smoke Point, °F				12.5			
ASTM Color							
RCR, W %							15.0
Vanadium, ppm	63						
Nickel, ppm	26						
Viscosity, SUS @210°F			177				
SFS @122°F			270		606		
SFS @210°F							166

DESULFURIZATION

Table B-10. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-250-14
Catalyst Age, BBL/LB	1.61
Feed	60-65% Demetallized Lloydminster Vacuum Residuum
HRI Identification No.	L-422
	(13.2 °API, 2.83 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	764
Liquid Space Velocity, $V_F/Hr/V_R$	1.21
Catalyst Space Velocity, B/D/LB	0.13
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3950
Hydrogen Consumption, SCF/BBL	420
975°F+ Conversion, V %	6.1

YIELDS	W %	V %
H ₂ S & NH ₃	2.22	
C ₁ -C ₃	0.66	
C ₄ -400	1.81	2.32
400-650°F	6.51	7.34
650-975°F	28.39	30.16
975°F+	61.06	61.02
Total	100.65	
C ₄ +	97.77	100.84
Gravity, °API		17.8
Sulfur, W %	0.94	

FRACTION, °F	Coll. Liq.	1BP- 400°F	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	2.0	98.0	7.3	90.7	30.0	60.7
Gravity, °API	17.6	50.2	16.9	31.0	14.5	21.7	12.6
Sulfur, W %			0.90	<0.03	0.96	0.19	1.41
Carbon, W %	86.95						
Hydrogen, W %	11.61						
H/C Atomic Ratio	1.60						
Nitrogen, ppm	3347						
Aniline Point, °F		121		127		167	
Flash Point, °F			430		485		
Pour Point, °F			35		55		
RCR, W %							13.9
Vanadium, ppm	43						
Nickel, ppm	34						
Viscosity, SUS @210°F			215				
SFS @210°F					39		

DESULFURIZATION

Table B-11. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-250-25
Catalyst Age, BBL/LB	2.89
Feed	60-65% Demetallized Lloydminster Vacuum Residuum
HRI Identification No.	L-422
Catalyst	(13.2 °API, 2.83 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	1980
Temperature, °F	760
Liquid Space Velocity, $V_F/Hr/V_R$	1.04
Catalyst Space Velocity, B/D/LB	0.11
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	5150
Hydrogen Consumption, SCF/BBL	520
975°F+ Conversion, V %	11.9

YIELDS

	W %	V %
H ₂ S & NH ₃	2.28	
C ₁ -C ₃	0.66	
C ₄ -400°F	1.93	2.47
400-650°F	7.18	8.04
650-975°F	31.04	32.85
975°F+	57.71	57.26
Total	100.80	
C ₄ +	97.86	100.62
Gravity, °API		17.3
Sulfur, W %	0.94	

FRACTION, °F	Coll. Liq.	IBP-400°F	400°F+	400-650°F	650°F+	650-975°F	975°F+
V % on Collected Liquid	100	2.3	97.7	8.0	89.7	32.7	57.0
Gravity, °API	17.2	50.7	16.1	29.7	14.6	20.8	11.3
Sulfur, W %		0.12	1.0	0.03	1.21	0.23	1.46
Carbon, W %	86.56						
Hydrogen, W %	11.70						
H/C Atomic Ratio	1.61						
Nitrogen, ppm	2665						
Aniline Point, °F		117		128		170	
Flash Point, °F			425		495		
Pour Point, °F			25		55		
RCR, W %							14.7
Vanadium, ppm	45						
Nickel, ppm	33						
Viscosity, SUS @210°F			223				
SFS @210°F					39		

DESULFURIZATION

Table B-12. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-251-4
Catalyst Age, BBL/LB	0.49
Feed	85% Demetallized Lloydminster Vacuum Residuum
HRI Identification No.	L-424
Catalyst	(16.4 °API, 1.88 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	761
Liquid Space Velocity, $V_F/Hr/V_R$	1.11
Catalyst Space Velocity, B/D/LB	0.12
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4720
Hydrogen Consumption, SCF/BBL	460
975°F+ Conversion, V %	14.6

YIELDS	W %	V %
H ₂ S & NH ₃	1.65	
C ₁ -C ₃	0.79	
C ₄ -400°F	1.18	1.50
400-650°F	10.30	11.38
650-975°F	34.29	35.63
975°F+	52.51	51.50
Total	100.72	
C ₄ +	98.28	100.00
Gravity, °API		19.0
Sulfur, W %	0.49	

FRACTION, °F	Coll. Liq.	IBP- 650°F	650°F+	650- 975°F	975°F+
V % Collected Liquid	100	12.7	87.3	35.7	51.6
Gravity, °API	18.9	31.7	16.1	21.4	12.8
Sulfur, W %	0.49	0.03	0.55	0.15	0.85
Carbon, W %	86.92				
Hydrogen, W %	11.96				
H/C Atomic Ratio	1.64				
Nitrogen, ppm	2495				
Aniline Point, °F		129		167	
Flash Point, °F			485		
Pour Point, °F			45		
RCR, W %					12.8
Vanadium, ppm	18				
Nickel, ppm	16				
Viscosity, SUS @210°F			259		

DESULFURIZATION

Table B-13. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-251-20
Catalyst Age, BBL/LB	2.44
Feed	85% Demetallized Lloydminster Vacuum Residuum
HRI Identification No.	L-424
Catalyst	(16.4 °API, 1.88 W % S) American Cyanamid Co-Mo
HRI No.	0.02" diameter beads 3104

OPERATING CONDITIONS

Hydrogen Pressure, psig	1990
Temperature, °F	760
Liquid Space Velocity, $V_F/Hr/V_R$	1.13
Catalyst Space Velocity, B/D/LB	0.12
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3670
Hydrogen Consumption, SCF/BBL	310
975°F+ Conversion, V %	8.0

YIELDS

	W %	V %
H ₂ S & NH ₃	1.49	
C ₁ -C ₃	0.53	
C ₄ -400°F	1.45	1.82
400-650°F	9.04	9.98
650-975°F	31.19	32.53
975°F+	56.79	55.48
Total	100.49	
C ₄ +	98.47	99.91
Gravity, °API	18.6	
Sulfur, W %	0.59	

FRACTION, °F	Coll. Liq.	1BP- 400°F	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	1.7	98.3	10.0	88.3	32.7	55.6
Gravity, °API	18.5	49.9	17.7	30.5	16.6	21.6	11.9
Sulfur, W %	0.59		0.63	< 0.03	0.69	0.20	1.02
Carbon, W %	86.85						
Hydrogen, W %	11.53						
H/C Atomic Ratio	1.58						
Nitrogen, ppm	3011						
Aniline Point, °F		119		129		167	
Flash Point, °F			385		470		
Pour Point, °F			20		50		
RCR, W %							14
Vanadium, ppm	20						
Nickel, ppm	24						
Viscosity, SUS @122°F			133				
SUS @210°F					246		
Smoke Point				12.0			